Alternative binders to simplify the recycling of lithium-ion batteries



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Submitted: 29/06/2023 Viva Passed: 16/10/2023 Word Count: 40521

<u>Abstract</u>

Alternative binders to simplify the recycling of lithium-ion batteries – Sean Scott

Binders are a vital component in the structure and function of battery electrodes. They do, however, have implications for the lifetime and recyclability or lithium ion batteries. This project identified several alternative binders that could simplify battery disassembly during end-of-life processing. Primarily anode binders were investigated, and it was found that water-miscible biopolymers, sodium alginate and gelatin, allowed complete delamination of the electrode active material from the current collector using low-powered ultrasound with water in 5 seconds. Modification of these polymers, with a deep eutectic solvent made from choline chloride and glycerol, also allowed for the enhancement of key properties such as the thermal stability, adhesive strength and, in the case of sodium alginate, the electrochemical stability of the cells at high cycling rates. Other polymer systems were also tested as binders to try and optimise other key characteristics of the anodes, such as the use of polyaniline and sodium alginate to form a polymer blend. Anodes created using these polymer blends found that the conductivity increased with polyaniline content, but other factors such as a poorer adhesive strength was observed.

Alternative extracellular adhesives and pack designs were also discussed, where a novel pack structure using a zigzag conformation of the cells joined together with pressure sensitive adhesives such as glue dots. This was shown to significantly reduce disassembly time and create a simplified dismantling procedure that could be easier to automate, increasing the economic viability of battery disassembly versus conventional end-of-life processes like shredding. This study included an environmental impact study comparing battery disassembly steps when alternative adhesives were used in both electrode binders and extracellular adhesives. These were then compared to commercial standards. This showed a 200% reduction in the global warming potential of the overall recycling process highlighting the importance of design for recycle for LIBs benefits, in terms of performance, economic viability of disassembly and environmental impact.

Parts of this work have already been published in the following articles:

Publications

S. Scott, J. Terreblanche, D. L. Thompson, C. Lei, J. M. Hartley, A. P. Abbott and K. S. Ryder, Gelatin and Alginate Binders for Simplified Battery Recycling, *J. Phys. Chem. C*, 2022, **126**, 8489–8498 (Chapter 3)

S. Scott, Z. Islam, J. Allen, T. Yingnakorn, A. Alflakian, J. Hathaway, A. Rastegarpanah, G. D. J. Harper, E. Kendrick, P. A. Anderson, J. Edge, L. Lander, A. P. Abbott, Designing lithium-ion batteries for recycle: The role of adhesives, *Next Energy*, **1**, 2023, 100023 (**Chapter 6**)

Two other papers are in preparation. (Chapter 4 & 5)

Conferences

S. Scott, J. Terreblanche, D. L. Thompson, C. Lei, J. M. Hartley, A. P. Abbott and K. S. Ryder, Gelatin and alginate binders for simplified battery recycling, Electrochem 2022 at University of Edinburgh, 5th September 2022

S. Scott, J. Terreblanche, D. L. Thompson, C. Lei, J. M. Hartley, A. P. Abbott and K. S. Ryder, Gelatin and alginate binders for simplified battery recycling, Faraday Early Career Researcher Conference, University of Warwick, 31st October 2022

S. Scott, Design for recycling: How using alternative binders can influence stability, performance and recyclability of lithium-ion batteries, Emerging Analytical Professionals Conference, Kettering, 13th May 2022 (Poster)

Statement of Originality

The experimental work detailed in this thesis has been carried out by the author in the Centre for Sustainable Materials Processing at the University of Leicester between September 2019 and June 2023. The work has not been submitted and is not presently submitted for any other degrees at this or any other institution.

Signed.....

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Acknowledgements

Firstly, I would like to thank my family; my grandparents, brother, aunt, uncle, and cousins especially for all their encouragement and support throughout the years, especially at my lowest points, I could not have done this without you.

I would also like to thank my friends, both back up in Yorkshire and here in Leicester for all of their advice, and laughter as well as the discord calls, tea breaks and pub trips needed to get me through this project.

A big thanks to my supervisors Prof. Karl Ryder and Prof. Andy Abbott for your continued guidance and support throughout this PhD. Thank you for providing this opportunity and plenty of others over the years that have been invaluable to me.

Thank you to the Faraday Institution for giving valuable training and opportunities to present this work and be part of a larger scientific community that I hope to contribute to further in the coming years.

"Do, or do not, there is no try" - Yoda

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List of Abbreviations

Gly – glycerol

EV – electric vehicle NaAlg - sodium alginate ICE – internal combustion engine PEG – polyethylene glycol GHG – greenhouse gas SEM – scanning electron microscopy Ni-MH – nickel-metal hydride EDX – energy dispersive X-rays AFM – atomic force microscopy LIB – lithium-ion battery LCO – lithium cobalt oxide PFT – peak force tapping ATR - attenuated total reflectance LMO – lithium manganese oxide NMC – nickel manganese cobalt oxide FTIR - fourier transform infrared IR – infrared NCA – nickel cobalt aluminium oxide LFP – lithium iron phosphate TGA – thermogravimetric analysis LCA – life cycle assessment DSC – differential scanning calorimetry EOL – end-of-life $L_{\rm C}$ – critical load PVDF – polyvinylidene fluoride 3DM – 3D microscopy CMC – carboxymethyl cellulose EC – ethylene carbonate SBR – styrene butadiene rubber PC – propylene carbonate PTFE – polytetrafluoroethylene EIS – electrochemical impedance spectroscopy NMP - N-Methyl-2-pyrrolidone R_{CT} – charge transfer resistance PANI – polyaniline R_{Sh} – sheet resistance CB – carbon black EB – emeraldine base SEI – solid electrolyte interface ES – emeraldine salt DES – deep eutectic solvent PSA – pressure sensitive adhesive ChCl – choline chloride GWP – global warming potential

Chapter 1: Introduction

1.1 Batteries for transportation

Batteries have played a fundamental part of automotive transportation since its development in the late 1800s. In fact, the majority of personal vehicles in cities were electric vehicles (EVs) until the 1910s when the mass-production of cars using internal combustion engines (ICEs), notably the Model T, became cheaper and more widely available.¹ Since then, batteries have found use in many other applications, such as in personal electronics and static energy storage. However, it is the re-emergence of EVs in the modern era, to combat rising greenhouse gas (GHG) emissions, that has significantly influenced the need for their continued development. These rechargeable batteries are based upon the initial energy storage device created by Alessandro Volta, dubbed the 'Voltaic Pile'.² This system consisted of two metal plates, one copper and one made of zinc and between these two plates was a cloth moistened with either vinegar or a brine solution, which acted as the electrolyte.² While the same general structure is used in contemporary batteries, the chemistry of the components have changed significantly. The notable battery chemistries that have been used in transportation are summarised and compared in the following section.

1.1.1 Lead acid batteries

The first form of rechargeable battery that became widely used is the lead acid battery, which was developed by Gaston Plante in 1859.³ Lead acid batteries generally use PbO₂ as the cathode active material and Pb as the anode active material, along with H₂SO_{4(aq)} as the electrolyte. A schematic diagram showing the general structure of a lead acid battery is given in **Figure 1-1a**. Lead acid batteries were used in the power train in the majority of the earliest EVs. As mentioned, these early EVs were the preferred form of personal transportation in urban environments due to their lack of emissions and noise pollution compared to vehicles powered by gasoline. However, this was short lived as the development of mass-produced ICE vehicles took over the majority of the market share. Lead acid batteries still saw significant use, most notably in ICE vehicles as the ignition source for the engines, which replaced the hand cranks used previously. Compared to modern EV battery chemistries, lead acid batteries possess inferior energy and power density, but have much simpler chemistries which has allowed for highly efficient and

economical recycling methods to be developed allowing recovery of ~ 99% of the battery components for reuse in new batteries.⁴ Due to this high recycling efficiency and the capability to remanufacture new batteries from legacy materials, a lead acid battery recycling approach, which will be discussed later, is often cited as the goal of recycling methodologies for the other battery chemistries.

1.1.2 Nickel-metal hydride batteries

Nickel-metal hydride (Ni-MH) batteries became increasingly prevalent in battery technology due to their better performance, compared to lead acid batteries, and were used to power some of the earlier modern EVs.^{5,6} Some of these improved characteristics include an ideal operating temperature, increased power and energy densities and an improved cycle life as shown in **Table 1-1**.⁶ Ni-MH batteries are successors to the nickel-cadmium battery, sharing a lot of the same characteristics, which are seen in **Table 1-1**. However, due to the toxicity of cadmium, Ni-MH became the main nickel-based battery as they were relatively safe to use.⁷ In a Ni-MH battery the anode active material is a metal hydride and the cathode is composed of nickel oxide hydroxide, NiOOH. The electrolyte is an alkaline solution, typically an alkaline hydroxide, often containing additives to enhance the battery performance.⁵ The most widely used electrolyte is KOH in H₂O with a LiOH additive.⁶ A schematic diagram for a Ni-MH battery is given in **Figure 1-1b**.



Figure 1-1: Schematic diagrams showing the general structure and overall redox reaction for two types of battery chemistry. a) lead acid battery, b) nickel-metal hydride battery

Despite the Ni-MH battery showing improved performance versus lead acid batteries they are inferior to lithium-ion batteries (LIBs), with a lower energy and power density, albeit with a similar cycle lifetime as shown in **Table 1-1**. Additionally, there are

numerous other issues that limit the use of Ni-MH batteries. These include numerous capacity-fading mechanisms such as high self-discharge rates, high internal temperatures and significant memory effects.⁸ Other limitations of this battery chemistry include the relatively high cost, due to the use of nickel, and the recycling rate compared to lead-acid batteries, due to the higher complexity in this battery chemistry, leading to only 50-60% recovery of battery components, often in forms unsuitable for repurposing into new batteries.⁹

1.1.3 Lithium-ion batteries

The first commercial LIB was patented in 1991 by Sony and was the accumulation of work by numerous scientists over the previous decades. The most notable of which were Whittingham, Goodenough and Yoshino who won the chemistry Nobel Prize in 2019 for their contributions to the development of the LIB.^{10,11} During development a lot of focus would be brought upon investigating many different lithiated transition metal oxides, for use as intercalation electrode materials. The first of these to be patented was LiCoO₂ (LCO), which was the cathodic material within the first commercial LIB produced by Sony. While LCO possesses a relatively high theoretical specific capacity (274 mAh.g⁻¹), good cycling performance and low self-discharge rate,^{12,13} it is only currently utilised as a cathodic material in personal electronics due to the low availability and high cost of cobalt and its poor thermal stability.^{14,15}

The decades following the commercialisation of the first LIB allowed for further development of the electrode materials. While the anodic materials remain largely similar, often being graphite based, many different lithiated metal oxides have been utilised. The most notable among which have been Lithium Manganese Oxide (LMO), Lithium Nickel Manganese Cobalt Oxide (NMC), Lithium Nickel Cobalt Aluminium Oxide (NCA) and Lithium Iron Phosphate (LFP). The different cathode chemistries will have an effect on certain battery properties and are often tailored based on the application. For instance, Nissan Leaf batteries prioritise energy density to increase the range of the vehicle, whereas the batteries used in Formula E focus more on power density to achieve better acceleration and top speed.¹⁶ It should also be noted that blends of different metal oxides and the ratios of the transition metals used in the mixed oxides, NMC and NCA, can be changed to affect battery properties, or most importantly, lower the cost of the battery by using less of the more expensive metals, i.e. cobalt and nickel.¹⁷

Table 1-1 summarises the key performance characteristics of all the different secondary batteries discussed in this section along with their respective electrode materials. LIBs have become the dominant battery technology for most applications due to the superior energy and power densities compared to lead acid and Ni-MH systems. However, there are still several significant limitations for LIBs, especially when used in EVs. Some of the key issues are related to the range and recharge time of the batteries as well as the significant onset cost of creating the batteries due to the nickel and cobalt content. Additionally, similarly to Ni-MH batteries, there are numerous issues surrounding the recycling LIBs, from a lack of cell standardisation to complex internal chemistries affecting the recovery of the battery components, leading to a similar recycling rate to that of Ni-MH of 50-61%.^{9,18}

Table 1-1: Summarising some of the key characteristics of the batteries that have commonly been used in electric vehicle applications. Ni-MH is nickel-metal hydride, LiCO is lithium cobalt oxide and LiNMC is lithium nickel manganese cobalt oxide.^{19–23}

Battery Type	Anode Material	Cathode Material	Nominal Voltage (V)	Energy Density (Wh/Kg)	Power Density (W/Kg)	Cycle Life (Cycles)
Lead- Acid	Pb	PbO ₂	2	35-40	250	200-1500
Nickel- Cadmium	Metallic Cadmium	Nickel Oxide	1.2	35-45	150-200	1000- 2000
Ni-MH	Metal Hydride	NiOOH	1.2	50-70	150-200	1000- 2000
LiCO	Li _x C ₆	Li _{x-1} CoO ₂	4.0	150	800	1000+
LiNMC	Li _x C ₆	Li _{x-1} NiMnCoO ₂	3.6-3.7	250-275	N/A	1000+

1.2 <u>Electrification of transport</u>

EVs, and in turn LIBs, have become increasingly important as governments around the world aim to limit the amount of GHG given into the atmosphere by implementing stringent emission targets. International collaboration agreements, such as The Paris Agreement are the main driving force behind these targets, and the UK, for example, aims to bring all GHG emissions to net zero by 2050 in order to meet these goals.²⁴ Transportation is the primary cause of GHG emissions in the UK, with around 27% of emissions coming from the various transport networks across the country. The electrification of transport has been identified as the primary method in which net zero emissions can be reached in this sector. The government aims to achieve this through a variety of policies, which include stopping the sale of petrol and diesel cars by 2035 and funding the research and development of future EVs.²⁵ The aim being to improve key characteristics such as the range and recharge time of the batteries while lowering production costs to make LIBs a more viable replacement to the ICE by the time sales of ICE vehicles cease in 2035.

As well as limiting GHG emissions, the electrification of transport will also minimise the UK's reliance on fossil fuels. This is especially important as reserves are quickly depleting and are due to run out in the next 50-60 years.²⁶ However, it is important to note that an increase in the amount of EVs will lead to an increased demand for energy production due to charging. Additionally, life cycle assessments (LCA) have found that electrification of transport can reduce GHG emissions by 65%, but only if the source of the electricity production is free of fossil fuels.^{27,28} Therefore, it is essential that the electrical infrastructure is also updated, to accommodate the increased energy demand and ensure that alternative energy sources, such as wind or solar, are utilised for the proposed targets to truly be met. However, even the use of these alternative energy sources do present some environmental concerns, mostly relating to the space required to meet demands.^{27,28}

The global adoption of EVs has been growing exponentially over the last decade, which is predicted to be a function of new legislation that will be coming into effect in the next few years, similar to the aforementioned UK legislation. According to the International Energy Agency the global stock of EVs reached over 26 million in 2022, 10 million more than 2021 and it is anticipated that, due to legislation changes, this number will continue increasing at an exponential rate for the next few years.²⁹ However, the electrification of transport does pose a risk to the existing automotive industries. In a report published by The Faraday Institution they stated that the health of the UK automotive industry would hinge on whether there were any large-scale battery manufacturing facilities, or gigafactories, within the UK. They also state that in order to facilitate the electrification of transport in the UK, without significant imports and maintaining a strong automotive industry, sustained investment in both research and

development as well as manufacturing facilities are essential.³⁰ In the instance where sufficient battery and EV manufacturing facilities are established, it is predicted that by 2040 1.8 million private and commercial vehicles will be produced in the UK, 95% of which will be EVs.³⁰ Another issue surrounding the increased adoption of EVs, is that as the number of EVs in circulation increases, a corresponding waste stream is produced. It is estimated that for every 1 million EVs sold, 250,000 tonnes of battery waste will be produced once they reach end-of-life (EOL).¹⁸ Given the aforementioned trajectory of EV sales, current waste processing and battery recycling routes will become overburdened in the near future, due to their relatively low processing capacity.³¹ Some companies are pledging to establish more widespread EOL EV treatment facilities to improve processing capacity, however current recycling processes are complex and inefficient mostly due to a lack of battery standardisation between manufacturers and car models. LIBs used in EVs use numerous cells connected in series to form the modules, which are then also connected in series or parallel to form the battery pack. The cell geometries used by a manufacturer will determine how many of each are used to form the battery. For example, the 2018 Nissan Leaf has 24 modules, housing 8 cells each. Currently there are 3 main types of battery cell design; pouch, cylindrical and prismatic.³² The structure of these cell designs, as well as an idea of how many cells and modules are needed to formulate each design are given in Figure 1-2.



Figure 1-2: Examples of different LIB cell types and how they are arranged into EV battery packs including how many cells and modules are required to create the modules and packs respectively.¹⁸

1.3 <u>Conventional lithium-ion battery recycling methodologies</u>

As previously mentioned, a significant concern for the increased adoption of EVs and LIBs is the amount of battery waste that will be produced once they reach the EOL. While research into battery chemistries and technologies capable of extending battery lifetimes is important, treatment of EOL batteries with the aim of creating a circular economy, where reclaimed battery materials are remanufactured into new batteries, is essential for the sustainability of EVs. As discussed previously, the recyclability of lead acid batteries is highly efficient and attaining a similarly effective LIB recycling procedure would be ideal in creating this circular economy. However, current LIB recycling processes are often ineffective and insufficient to treat the volume of EOL batteries that are currently produced, with a significant amount of these waste batteries being disposed of in landfill. Additionally, these procedures are often limited in scope, focusing on the recovery of cobalt and nickel, as the most valuable materials, while ignoring or downcycling the other components, such as aluminium, copper, lithium and graphite.³³ Commercial processes often use a combination of recycling methodologies in order to maximise the yields of the desired metals. The main methods being pyrometallurgy, hydrometallurgy and direct recycling. While these processes focus mostly on the recovery of cathode materials, ignoring the reclamation of graphite, a brief summary of each methodology and any necessary pre-treatment steps will be given in this section after a summation of lead acid battery recycling and why it is effective.

1.3.1 Lead acid battery recycling

Lead acid batteries are currently the only form of battery chemistry to achieve an efficient recycling scheme with a near 100% recovery rate. The toxicity and environmental impact of the lead acid battery components are what drove a large amount of development into recycling processes, as treatment and reuse of these batteries diminished the risks associated with emissions of components such as lead. **Figure 1-3** gives an overview of the entire closed-loop recycling procedure for lead acid batteries. The main reasons for the recycling rates being so high is the consistency in materials used by all the lead acid battery manufacturers and the relatively simple chemistry compared to battery types like Ni-MH and LIBs, allowing all lead acid batteries to undergo the same recycling process.³⁴ Additionally, lead acid battery recycling is a closed loop processes, which enhances the economic benefits as the onset costs of manufacturing new lead acid batteries are diminished as new raw materials are not required. This closed-loop system is the ultimate goal for research into the recycling of EOL LIBs, however due to the diversity in both cathode material and cell/pack design this is a lot more complex, as will be discussed in this section.³⁴



Figure 1-3: Overview of the lead-acid battery recycling scheme.³⁵

1.3.2 Pyrometallurgy

Pyrometallurgical processes employed in LIB recycling use high temperature furnaces (~700°C) to reduce metal oxides into alloys of cobalt, iron, nickel and copper.¹⁸ A major benefit of pyrometallurgy is that it can be applied to all types of LIBs indiscriminately without the need of pre-treatments. However, the recycling efficiency is relatively low with some crucial materials such as aluminium, manganese and lithium being lost in the slag phase. Hydrometallurgical techniques can then be used to reclaim these lost metals, or alternatively they could be downcycled for usage in other industries.^{18,36} Additionally, hydrometallurgy would be necessary to separate the metals

present in the alloy phase, which would be needed if battery precursors were to be formulated by the methodology. The increased cost and time requirements for the additional treatments will reduce profitability of the overall process. Therefore, downcycling of these materials into other uses, rather than reforming battery grade materials, is often preferred to maximise the economic viability of the process.

Pyrometallurgy also presents several environmental issues. The usage of high temperatures will lead to a significant energy consumption, which, depending on the way the electricity is generated, can have a substantial environmental impact and associated carbon footprint. Additionally, during processing some components of the LIB such as the electrolyte and the fluorinated binder will thermally decompose to form toxic gases such as HF and CO.^{18,37,38} Despite the environmental issues, high energy usage and the poor recovery of desired materials, this process is still widely utilised for the extraction of cobalt and nickel from LIBs, even though the resulting forms of these metals cannot be used in remanufacturing of new batteries to create a circular economy.³⁹

1.3.3 Pre-treatments

The initial pre-treatment process is the controlled discharge of the battery. This is done before the other recycling methodologies to reduce the risk of thermal events caused by contact between the anode and cathode during processing. Controlled discharge is particularly important for processes that separate battery components after shredding them, such as direct recycling routes that will be discussed in section 1.3.5. There are a few different methods used to discharge LIBs, Ohmic discharge where the battery is discharged through a load-bearing circuit or 'brine' discharge where the battery is discharged through a salt solution.¹⁸ The latter process can use different solutions for slightly different results. For example, halide salts will corrode the battery terminals allowing water into the cells and passivating the internal chemistries, whereas alkali metal salts do not exhibit as much corrosion which could mean the cells can be assessed and, where possible, re-used after discharge.⁴⁰

The most common form of recycling pre-treatment is a shredding or crushing step. In these steps a EOL battery is fed into a shredder in the presence of an inert gas such as nitrogen, carbon dioxide or argon.¹⁸ This process produces shredded 'black mass' as a feedstock for hydrometallurgy where the comminution aids in improving the recovery of metals via the solvents and works to decrease processing times. However, this feedstock is now highly contaminated with all the different battery components, requiring the use of complex chemistries and physical processes in order to produce usable waste streams. Some degree of physical separation of the black mass can be carried out to try and reduce the levels of contamination by exploiting changes in properties such as ferromagnetism, density and hydrophobicity between the components. However, these are often limited in their effectiveness. Shredding is often considered to be the responsible factor in the relatively poor performance of the subsequent recycling processes resulting in low purities and yields of the desired metals.^{18,39,41}

1.3.4 Hydrometallurgy

Hydrometallurgy utilises aqueous solutions to leach metals from the cathode material. Common leaching solutions consist of a combination of H₂SO₄ and H₂O₂ but other possible solutions using HCl and HNO3 to recover metals such as cobalt and lithium have also been explored.^{42–45} The effectiveness of these processes are dependent on the feedstock from the shredding step. As previously discussed, the 'black mass' has a high level of contamination as it contains all of the battery components. This means that multiple complex chemical and physical steps are required during processing and the final products may also be contaminated. Contamination of the end products would result in a reduced market value and can have an impact on their electrochemical performance if remanufactured into new battery materials.^{18,46} Hydrometallurgical techniques also use a large quantity of solvents, this can lead to the production of a significant amount of waste that will need to be treated, increasing the cost and environmental impact of processing. Additionally, some of these solvents are toxic or can decompose to produce toxic gases. For instance, the usage of H₂SO₄ and HCl can produce sulphur trioxide and chlorine respectively. Furthermore, many of the established procedures are only designed for specific battery chemistries. This means that in order to recycle batteries from different manufacturers, and even different vehicles, several processes would have to be in operation simultaneously, driving up the cost and processing time.^{33,47} While hydrometallurgy is capable of recovering a wider variety of the desired metals from cathode materials, it is limited by the feedstock, which increases the processing time, chemical complexity and lower purity products. Development of an alternative pretreatment step capable of quickly dismantling the battery packs and separating battery components to formulate purer waste streams would simplify the required chemical processing and make hydrometallurgical processing more viable. Figure 1-4 gives a

summary flowchart for both the pyrometallurgical and hydrometallurgical steps discussed along with the key outputs from each process.



Figure 1-4: A flowchart showing the typical steps and main outputs for pyrometallurgical and hydrometallurgical recycling methodologies for lithium-ion batteries.

1.3.5 Direct recycling

While pyrometallurgy and hydrometallurgy are the most widely used recycling techniques, other methodologies, such as direct recycling routes are also possible. Unlike hydrometallurgy, direct recycling aims to separate and reconstitute electrode materials from the black mass obtained from shredding without chemical processing steps.¹⁸ Similar to the physical separation steps used in hydrometallurgy pre-treatments, physical attributes such as ferromagnetism, density and hydrophobicity are used to separate battery components.¹⁸ Like with hydrometallurgy multiple steps are often required. These include magnetic separation, crushing, filtering and shaker tables to produce two main factions, a fine faction containing the electrode coatings and another, coarse faction, containing the casing materials and current collectors.⁴⁸ These factions can then be treated to further isolate the different materials found within. The coarse fraction can undergo magnetic

separation to remove steel casings, as well as density separation to disassociate the plastic and the foil.¹⁸ Meanwhile, the fine fraction is subjected to froth flotation to remove the hydrophobic carbon from the more hydrophilic metal oxides.⁴⁹ It should be noted that methods similar to pyrometallurgy and hydrometallurgy would still need to be employed in order to remove the binder from the electrode coating faction.^{46,50,51} Although, as was the case with hydrometallurgy, if an alternative pre-treatment step capable of effective separation of all the battery components to formulate pure waste streams was developed, it would remove the need for the majority of these separation steps.

1.3.6 Umicore case study

A major example of a commercial LIB recycling procedure that utilises some of the methodologies outlined above is the Umicore process carried out in a facility in Belgium. Pyrometallurgical processing forms the basis of the technique, mostly to remove the need for any pre-treatments, and hydrometallurgical steps are then used to isolate nickel and cobalt to form an alloy.^{32,52} Presently, this process treats around 7,000 metric tons of battery waste per year, which is the equivalent of 250,000,000 mobile phone batteries or 35,000 EV batteries.⁵³ Also, to accommodate the increasing market share of EV batteries within Europe, Umicore have invested £25 million to increase this capacity further in the coming years. However, many more facilities would be required to meet the predicted demand for waste battery treatments. Despite Umicore being one of the few major battery recycling plants in the world, the process possesses several issues. As this process is pyrometallurgy-based is has the same problems mentioned above surrounding the sole focus on cobalt and nickel recovery and ignoring other components, such as lithium, that are lost in a slag phase.³² Furthermore, this process requires the input of Li₂CO₃ meaning that there will be an even greater total loss of lithium overall.^{32,54} It should be noted that routes to recover the other components are possible and have been explored, for example, Umicore have outlined a process to recover the majority of the lithium in the form of LiCO₃ via precipitation with NaCO₃. However, this step, as well as others targeting less valuable components in LIBs were not considered economically viable and would reduce the profitability of the overall procedure.³²

In summary, conventional recycling procedures focus on cathode recovery, due to the relatively high value of cobalt and nickel. Additionally, the forms of these metals that are produced are often not suitable to reintroduced into new batteries due to contamination and a lack of purity. However, new legislation, such as updates to the battery directive from the European Union, has begun to require a higher recycling rate for LIBs and that new batteries need to be manufactured using a greater amount of reclaimed material.⁵⁵ This means that the development of novel processes able to target all battery components, including the graphite anode, needs to be developed. Also, the development of low cobalt batteries to save battery manufacturing costs will significantly reduce the profitability of recycling methodologies that focus on its recovery, such as the Umicore process.⁵⁶ Therefore, future LIB recycling processes need to be capable of creating high value battery grade materials, via a fast and cheap procedure, to maintain economic viability, fulfil legislative requirements and establish a circular economy.

1.4 <u>Future prospectives for lithium-ion battery recycling</u>

An ideal recycling process would allow efficient and simple recovery of all the materials used in LIB manufacturing, in a form that can be reprocessed into new battery materials.⁵⁷ Such a process would reduce the amount of waste being produced by the battery industry as well as reducing the cost and environmental impact of manufacturing new batteries, as legacy materials would be incorporated. Some issues facing potential commercial recycling schemes have already been touched on, this section aims to summarise these key issues that need to be resolved and some routes that have been identified that could achieve this.

1.4.1 Legislative issues

Despite this study focusing on alternative binders and battery recycling processes, it is important to briefly touch on legislative changes that can be made to push forward the development of novel recycling and reuse techniques. Current legislation, such as the EU battery directive is limited in scope, only setting defined recycling rates for lead-acid and Ni-MH batteries. LIBs are classed as 'other batteries' and have a minimum acceptable recycling rate of 50% by weight, which means that EV and LIB manufacturers can follow these rules by recycling the steel battery casings and ignoring the critical materials within the cells.⁵⁸ This directive is due to be updated to increase the minimum recycling rate of LIBs and enforce that a minimum amount of reclaimed materials, such as nickel and lithium, need to be used in new batteries. However, these requirements are still low, for example, only 6% of the lithium and nickel in new batteries would be required to be from EOL sources in the updated legislation.⁵⁵ The fact remains that it is still largely the choice

of the EV or LIB manufacturers whether or not to recycle and reclaim the majority materials present within the batteries. In most cases this choice is determined by the profitability of the recovered products or the cost savings to manufacturing that can be made by reusing materials recovered from EOL sources. Due to the limitations in the current methodologies outlined above, most companies choose to just fulfil the minimum legislative requirements, which is why there is a push by some in the industry to set increasingly stringent targets.

Legislation surrounding the storage and transportation of LIBs is also significant when it comes to recycling, especially in the UK. Currently, there are no large-scale recycling facilities based in the UK, instead recycled EOL batteries are shipped overseas to companies such as Umicore. Therefore, it is imperative to build UK-based recycling plants for LIBs as the transportation and long-time storage of these batteries does present safety risks, with significant costs associated with legislative restrictions and safety precautions.⁵⁹ Additionally, the establishment of UK-based recycling facilities could entice other major battery and EV manufacturers to the UK in order to minimise the cost of transportation of waste batteries. However, this is still largely based on the effectiveness of the recycling procedures in order for such facilities to be commercially viable and novel recycling techniques are imperative to create such processes.

1.4.2 *Design for recycle*

From the issues discussed with hydrometallurgy it was determined that the process feedstocks, obtained from shredding, are often the limiting factor in the effectiveness and efficiency of recycling. In order to improve the quality of these feedstocks, effective dismantling and separation of battery components from the pack down to the cell level would be required. These processes are often complicated due to the internal design of the batteries. With aspects such as the packing of the cells, the type and formation of the connectors used in the casings and any chemical or physical damage made to the components during battery usage all contributing to the difficulty of dismantling procedures.^{60,61} Additionally, vehicular LIBs use an extensive amount of structural adhesives on the pack level, to provide strength to the system and minimise the movement of cells during use that could lead to defects and premature failure.⁶² The complexity of the designs, as well as the excessive use of structural adhesives in current LIBs, significantly diminish the economic viability of dismantling the battery prior to separation

steps over contemporary pre-treatments such as shredding, regardless of the benefits surrounding the formation of purer waste streams. In a recent study, it was found that disassembly procedures are only viable when automated, however, this is currently not possible due to the aforementioned complexity in battery designs.⁶³

So, in order to create a more effective recycling methodology, which is capable of forming battery grade materials from separate, pure waste streams, novel battery designs and alternative extracellular adhesives that will facilitate EOL disassembly are required. One such approach could be changing the geometries of the tab connectors, which are used to connect electrodes to one another. **Figure 1-5** shows an example design that could be utilised to simplify cell disassembly, where the stacks of anodes and cathodes can be pulled apart easily after the battery is opened.⁶⁴ An aspect of this project investigates another design with a similar principle and how this design and alternative adhesives, can create a viable automated disassembly procedure as a more appropriate precursor to techniques such as hydrometallurgy.



Figure 1-5: A schematic diagram showing a proposed redesign to battery packs with an alternative electrode tab alignment. Dashed lines show potential cut points to open the battery and the arrows show how the electrodes are separated.

Design changes to LIBs that can aid in battery recycling during separation pretreatments are not limited to pack level alterations. As using alternative components within the electrodes, specifically the binders, can be exploited to allow for more efficient delamination of the electrode materials at the EOL. The binder is responsible for holding the electrode components together and keeping them adhered to the current collector. This makes the failure mechanisms and decomposition of the binder imperative to new recycling procedures aiming to separate all the cell components into distinct waste streams.

1.5 <u>Electrode binders</u>

As stated above, binders are polymeric materials used within the LIB electrodes to hold the active materials together and to adhere the active material to the current collectors. This also works to reduce internal resistance by promoting interconnectivity between electrode components.⁶⁵ Interactions occur between these components during slurry mixing via two mechanisms: direct binding, where the binder is physically adsorbed to adjacent particles forming interparticle bridges; Figure 1-6a gives an example of this binding mechanism for a gelatin binder. The other mechanism is via indirect binding, where the polymer forms a chemical inert network which captures the particles, seen in Figure 1-6b for a polytetrafluoroethylene (PTFE) example system.⁶⁶ Sufficient dispersion of particles is also imperative in the formation of homogeneous slurries and is dependent on numerous factors to promote electrostatic repulsion such as the density, flexibility and the polarity of polymers. Controlling binder adhesion and distribution is also essential. This is because if the distribution of the binder is not uniform, the adhesion between the active material and the current collectors can deteriorate and rupture the electrode.67,68 Usage of appropriate solvents for a given polymer facilitates dissolution and aids in the dispersion of particles within the slurries. For instance, the conventional polyvinylidene fluoride (PVDF) binder possesses a high dipole moment so polar solvents, such as N-methyl-2-pyrrolidone (NMP), are necessary to dissolve the polymer and resist flocculation during electrode manufacturing.⁶⁵



Figure 1-6: Diagrams of two possible binding mechanisms for composite electrodes, using graphite anodes as an example. a) Direct binding - adsorption of particles to form interparticle bridges, b) Indirect binding - polymer network is formed and 'traps' active material particles.

PVDF is used as a binder due to its inherent thermal, chemical and electrochemical stability, as well as its oxidation resistance and adhesive properties, which can enhance the longevity of the battery. The structure of PVDF involves a polymer backbone with alternating CH₂ and CF₂ groups. Different conformations of PVDF are based on the arrangement of these functional groups and will alter several important qualities such as the dipole moment and pyroelectric activity. **Figure 1-7** shows the main PVDF conformations. Despite the benefits and widespread use of PVDF, the usage of NMP to formulate the electrode slurries during manufacturing and de-bind the binder component during recycling processes presents issues. As a toxic, flammable and volatile solvent, the use of NMP will drive up the environmental and economic cost of battery fabrication.⁶⁹ Furthermore, the properties that make PVDF a good binder will have a negative impact on the recyclability as its stability and adhesion characteristics make separating the electrodes to create purer waste streams difficult.



Figure 1-7: Different chain conformations of PVDF responsible for stability and adhesion properties.⁶⁵

As discussed previously, to counter some of the problems with using PVDF, alternative water miscible binders have been incorporated into LIBs, primarily into the anodic materials. The use of carboxymethyl cellulose/styrene butadiene rubber (CMC/SBR), compared to PVDF, lowers polymer and solvent costs, improves environmental and safety concerns by removing the need for NMP and have even been found to be more accommodating of the larger volume expansion associated with anodes during cycling.⁷⁰ Additionally, it is the exceedingly high stability of PVDF that is a key contributing factor for the need of high temperature pyrolysis steps in current recycling schemes. It is thought that alternative binder materials can allow for more effective separation of cell components using much milder conditions.¹⁸

1.5.1 <u>Alternative binders</u>

The use of water miscible binders, similar to CMC/SBR are commonly investigated due to the replacement of NMP with water during electrode manufacturing.⁷¹ However, alternative binders, also present improved characteristics compared to the current materials. For instance, gelatin and chitosan possess improved flexibility compared to PVDF to better accommodate volume expansion during charge/discharge and come at a lower cost to CMC/SBR. Furthermore, polymers such as sodium alginate (NaAlg) have been investigated in a variety of contemporary and next-generation battery chemistries, such as in graphite anodes, silicon/graphite anodes, lithium-sulfur cathodes and lithium titanate (Li₄Ti₅O₁₂) electrodes.⁷²⁻⁷⁷ Where improvements could be seen in the electrochemical performance, with regards to higher capacities, improved coulombic efficiency and lower impedances when compared to traditional polymers like PVDF. These benefits were brought about by the ability of the alginate to form hydrogels and cross-link with foreign ions like Zn^{2+} and Ca^{2+} , enhancing the interconnectivity of the electrodes and improving the diffusion and reversibility of lithium-ion transport.^{76,77} Modification of these binders has also been explored to further enhance in-operando performance and stability whilst retaining these manufacturing benefits.^{78,79} Additionally, conjugated polymers such as polypyrrole, polyaniline (PANI) and polythiophenes such as 3,4-ethylenedioxythiophene (PEDOT) have been researched in a bid to improve the conductivity and electrochemical stability of the electrodes.^{80,81} While polymers like PEDOT has shown exceptional electrochemical characteristics it is too expensive for commercial application into LIBs and more reasonably priced polymers, like PANI, are gaining more attention.⁸²

It is important to note that the majority of the research into water miscible binders is limited by the electrode active materials. For example, metal oxide cathodes experience extensive cracking and poor adhesion when these polymers are used. This is due to lithium from the metal oxide being leached by the water within the slurry and corroding the aluminium current collector during manufacturing resulting in gas evolution.^{83–85} It is clear that further research is necessary to determine ideal binder systems that can retain the stability and performance of the electrodes, regardless of the chemistries used, which can also aid in the recyclability of the LIBs when they reach the EOL. Current cells, using PVDF, require intensive conditions or solvents to remove the binder, which is why shredding and pyrolysis are preferred over dismantling of the battery during recycling

pre-treatment steps. Alternative binders, as well as reducing the environmental and economic impact of manufacturing, have the potential to significantly reduce the complexity and environmental impact of recycling procedures and the aim of this present investigation is to develop alternative binder materials, with novel modifications, that can fulfil these aims and can optimise performance and stability of the anodes. A summary of the other components present within LIBs are given in the section 1.6.

1.6 Structure and chemistry of the lithium-ion battery

This section aims to provide a more detailed discussion of battery chemistry, as well as the components within the battery, their structure and how the batteries are manufactured. Generally, a LIB will be made up of the following components: a negatively charged electrode (anode), a positive charged electrode (cathode), a polymeric binder, a conducting additive, a separator, a lithium salt electrolyte and electrolyte additives. As briefly discussed in section 1.1, each of these components, especially the cathodic materials, will have various chemistries based on the manufacturer and the desired use of the battery. **Table 1-2** shows the most common materials used in each of the aforementioned components. It should be noted that while there are different categories of electrode materials, based on how the lithium ions interact, this study focuses solely on intercalation materials. These materials are lattice structures with interstitial sites that can host the lithium ions without significant disruption to the structure.⁸⁶

Battery Cell Components	Common Materials Used
Anode active material	Carbon rich materials e.g. graphite, silicon
Anode foil	Copper
Cathode active	Layered Structures; e.g. LiCoO ₂ (LCO), Li(Ni _x Mn _y Co _{1-xy})O ₂ (NMC), Li(Ni _{1-x-y} Co _x Al _y)O ₂ (NCA)
material	Spinel Structures; e.g. LiMn ₂ O ₄ (LMO)
	Olivine Structures; e.g. LiFePO4 (LFP)
Cathode foil	Aluminium
Binder	Polyvinylidine fluoride (PVDF), carboxymethyl cellulose (CMC), styrene butadiene rubber (SBR)
Conductive additives	Carbon black (CB), carbon nanotubes
Separator	Polyethylene, polypropylene
Electrolyte	Ethylene carbonate, propylene carbonate, dimethyl carbonate, ethyl methyl carbonate
Conductive salt	Lithium hexafluorophosphate (LiPF ₆)
Electrolyte additives	Vinylene carbonate, phenylcyclohexane, and fluoroethylene carbonate

 Table 1-2: Common materials used in the different components within a lithium ion battery.

 battery.

The electrode materials, the graphite and lithiated metal oxides, are the active materials because their interactions with the lithium ions via a reversible redox exchange, are responsible for converting chemical energy into electrical energy so the battery can operate.⁹⁰ Batteries are formed in a 'discharged' state due to the usage of the lithiated metal oxides. When charged, a voltage will be applied across the electrodes, allowing current (electrons) to flow. To ensure charge neutrality is maintained, a lithium ion is liberated from the cathode and will migrate through the electrolyte, intercalating into the anode between the graphite layers.⁸⁸ During discharge the opposite will occur with the electron generated, flowing around an external circuit in order to provide work to external

systems.⁸⁸ Figure 1-8 shows a schematic diagram of a LIB showing the movement of lithium ions between the electrode materials during charge and discharge. Additionally, Equations 1-1 and 1-2 show the relevant redox reactions occurring at the anode and cathode respectively.



Figure 1-8: A schematic representation of a lithium-ion battery, showing the movement of lithium ions during charge and discharge into the intercalation electrode materials, typically a lithiated metal oxide for the cathode and graphite for the anode.

$$\operatorname{Li}_{x}C_{n(s)} \longrightarrow x \operatorname{Li}^{+}_{(soln)} + x e^{-} + nC_{(s)}$$
(1-1)

 $Li_{1-x}MO_{2(s)} + xLi^{+}_{(soln)} + xe^{-} \checkmark LiMO_{2(s)}$ (1-2)

The 'M' term relates to the transition metal(s) within the cathode. Discharge is seen from left to right and charging is occurring from right to left in both equations.

1.6.1 Manufacturing

Before providing detail of the other key battery components, a brief introduction into cell manufacturing will be given, based primarily on the pouch cell as an example. Regardless of the type of battery cell, the first step of the manufacturing remains the same, the creation of the electrodes. A schematic diagram of the electrode formation is given in **Figure 1-9** with the main steps for electrode formulation and their incorporation into a battery pack being detailed below:³²

- 1. The electrode materials, such as the active material, carbon based conductive agent and the binder solution (NMP solution containing PVDF), are mixed together into a slurry. This slurry is stirred thoroughly to ensure homogeneity.
- 2. The slurry is then coated onto the metal current collector using a doctor blade, to ensure that the thickness is carefully controlled.
- 3. After coating, the current collector is passed through an oven in order to evaporate the solvent.⁹¹
- 4. Using a calenderer, the dried electrode is compressed to produce a continuous thin foil and to increase the density of the electrode mass.
- 5. The foil is then slit to the desired cell dimensions and connection tabs are attached to the electrodes, in order to provide an electrical contact to the relevant terminals.



Figure 1-9: Schematic representation of the fabrication of the electrodes.³²

- 6. Electrodes are stacked alternately, separated by the presence of an endless z-folded separator membrane.
- 7. Once finished, the stack is taped and the electrode terminals are created by ultrasonically welding the electrode tabs together.
- 8. The stack is then inserted into an aluminium laminated multilayer foil case. The case is then heat sealed on all sides, bar one.
- 9. The cell is then tested for any internal short circuits before any residual humidity is removed via heating with a vacuum dryer.
- 10. The unsealed side is then utilised for filling the cell with electrolyte before the cell is vacuum sealed using a two-chamber configuration.
- 11. Once sealed, the cell will undergo an initial charge, so the solid electrolyte interface (SEI) layer can form at the anode. This will also cause gas evolution, which can result in cell inflation and ionic contact loss. To combat this, a second chamber is used to collect gas released by the cell. Once the gas is collected the cell is resealed.
- Once a cell is finished, multiple tests are conducted, including X-ray inspections before the battery is put into storage.⁹²
- 13. While in storage the batteries undergo a testing period, where the voltage is recorded at regular intervals over this time to test for the presence of micro circuits.

1.6.2 Cathode

Despite this project focusing on the anodic materials, discussion of the cathode is important at this stage. This is because the overall capacity of the LIB is often dependant on the cathode, as such, the majority of LIB research focuses on this component. As stated previously the cathode material in a conventional LIB system consists of a transition metal oxide active material coating an aluminium foil. The most notable examples of cathode materials include NMC, LFP, LMO and NCA. Transition metal oxides, such as these, typically fall into one of three main crystal structure categories, layered, olivine and spinel, the general crystal structures of each are given in **Figure 1-10**. The crystal structure of the cathode will lead to changes in many key attributes such as electrochemical stability and thermal stability and even have a notable impact on where the lithium ions are situated in the structure and the way they move within the electrodes.⁹³



*Figure 1-10: Examples of intercalation cathodes with the layered, spinel and olivine structures.*⁹³

Stability changes within each type of cathode crystal structure are usually a function of the movement of lithium ions during charge and discharge. In 'layered' structures, such as LCO, the transition metal and lithium ions occupy oxygen octahedral interstitial sites in alternating layers.^{14,94} In these structures lithium extraction during cathode discharge is limited to 50%, so for LCO with a theoretical capacity of 274 mAh.g⁻¹ only around 140 mAh.g⁻¹ is attainable. This is because further de-lithiation of the cathode will lead to repulsive interactions between oxygen anions causing lattice distortions and cracking of the cathodic material.^{95,96} 'Spinel' lattice structures, like those seen in LMO cathodes, have manganese and lithium ions will occupying the octahedral and tetrahedral interstitial sites of a cubic close-packed oxygen lattice respectively.^{97,98} The volume changes of a spinel cathode as a result of lithiation and de-lithiation shows greater deviation than the volume changes for layered structures (~3% for layered vs. 3.2% for spinel). This is believed to be caused by a change in the oxidation state of manganese causing phase changes leading to Jahn-Teller distortions, with these distortions also capable of contributing to electrode stresses and could compromise the mechanical integrity of the electrode.⁹⁸ For 'olivine' materials, such as LFP, where the crystal lattice is a distorted hexagonal close-packed oxygen network with lithium and iron (II) ions occupying the octahedral interstitial sites and phosphorous ions occupying the tetrahedral ones.¹⁴ Unlike the previous crystal structures, olivine structures maintain the same lattice configuration maintaining structural integrity throughout charge and discharge.^{95,96} However, because both lithiated and de-lithiated crystal structures remain the same the associated volume

expansion during charge and discharge is also the largest of the 3 types at approximately 6.8%.⁹⁵

EV batteries mostly utilise polycrystalline mixed transition metal oxides as their cathode materials, namely NMC or NCA.¹⁴ Using these cathodes over single crystal structures, such as LCO, allow for the intrinsic properties of each metal to enhance the resulting cathode in different ways. For example, the use of nickel results in a slightly higher attainable capacity of between 150-170 mAh.g⁻¹ for NMC, versus 140 mAh.g⁻¹ for LCO.^{88,99} While the use of manganese will improve the thermal stability and safety of the cathode compared to LCO, as thermal runaway is no longer a risk at relatively low temperatures of 200°C for NMC as it is in LCO.¹⁴ Additionally, the cost of the cathodic material will be reduced as the overall usage of critical and expensive metals such as cobalt and nickel will be relatively low compared to equivalent cells using LCO and LMO respectively. Reduction in cobalt usage will also minimise the socio-political issues with sourcing cobalt for battery manufacturing.¹⁰⁰ NCA replaces the manganese component from NMC with aluminium, this maintains thermal stability, enhances the cycle life and maintains the same crystal structure during lithiation and de-lithiation, similarly to LFP.^{101,102} However, use of polycrystalline materials does present some issues primarily from anisotropic lattice expansion and shrinking during charge and discharge and poor volumetric energy density both of which can limit cycling stability and performance.¹⁰³

As stated previously, new cathode materials are the subject of a lot of LIB research with the aim of improving the amount of lithium ion extraction whilst retaining stability, and further reductions in the use of expensive metals like cobalt. Additionally, blending of mixed transition metal oxides with spinel structures such as LMO have been investigated and adopted in commercial LIBs to achieve similar goals.¹⁰⁴ However, it should be noted that as cathode chemistries become increasingly diverse, between both manufacturers and even different car models of the same manufacturer, it poses a significant challenge to EOL processing. This necessitates the use of complex chemistry to recover these materials and makes a standardised recycling procedure less feasible.^{32,94,105}

1.6.3 *Anode*

Commonly, an anode consists of a copper current collector coated with graphite as the active material.³² Graphite exists in a layered arrangement with layers of graphene sheets associated with each other via Van der Waal (vdw) interactions. The presence of two types of C-C bonding, covalent within the graphene sheets and vdw between the sheets, allows for graphite to be an excellent intercalation material, capable of accepting lithium ions into the structure. Anodes containing other materials, such as silicon, are also being studied, due to a higher theoretical capacity of silicon versus graphite (4200 mAh.g⁻¹ versus 372 mAh.g⁻¹), but graphite remains the popular choice at present due to the low cycling stability of silicon.¹⁰⁶ **Equation 1-1** outlines the charge and discharge reaction occurring at the anode, where the maximum stoichiometry of lithiated graphite is shown to be LiC₆, giving the aforementioned theoretical capacity of 372 mAh.g⁻¹.³² Despite the relatively low capacity, graphite possesses exceptional cycling and mechanical stability even though the volume expansions during lithiation is often much higher than that seen in the cathode materials.⁶⁷

Graphite morphology is an important aspect of the anode primarily due to how the morphology affects the surface area and the impact this has on critical processes during formation cycles and battery usage as a whole. **Figure 1-11** shows the key graphite morphologies that have been used in anodic materials, including flaked and spherical graphite. Flaked graphite are layers of graphene sheets with exposed basal and edge planes, while spherical graphite is a manufactured particle where the majority of the edge planes are shielded internally, with only a few exposed on the sample surface.



Figure 1-11: A diagram showing the different possible graphite morphologies that have been used in lithium-ion battery anode materials.

It is the availability of graphite edge planes that will change the surface area of the anode, dictating the behaviour and stability of the material. Particles with a higher amount of available edge planes, such as flaked graphite, will possess a higher surface area. These particles will facilitate easier lithium intercalation, but a greater amount of lithium will be lost during the creation of passivation layers during the formation cycles. Reducing the surface area minimises this irreversible loss of lithium but will decrease the power density of the cells as lithium intercalation routes are limited.¹⁰⁷ Spherical graphite is widely used in LIBs as it is considered a suitable compromise, able to provide a decent power density and minimising the lithium lost during battery formation cycles. Despite this, it should be noted that the cost of producing spherical graphite is three times more expensive than sourcing flaked graphite. While this cost is relatively low compared to the value of the cathodic components, there is an economic push for some manufacturers to incorporate more natural graphite into the anodic materials.¹⁰⁸ Reclamation and reuse of spherical graphite from EOL sources could also reduce these costs. However, as has been discussed previously, most current recycling processes focus solely on cathode metal recovery.

1.6.4 Electrolyte and solid electrolyte interface (SEI) layer

Electrolytes are typically solutions of organic carbonate solvents, additives and a conductive salt, which is often LiPF₆. Effective electrolytes are required to possess several characteristics, including: high thermal and electrochemical stability, high ionic conductivity, capable of forming a good SEI layer upon the anodic surface, relatively low molecular weight, be non-toxic and have a relatively low cost.^{109,110} The conductive salt, LiPF₆ is used to increase ionic conductivity by providing additional lithium ions to the system, shortening the diffusion pathway required for lithium ion transport between the electrodes. Carbonates are often utilised in LIB electrolytes due to the electronegative atoms present within its structure, which promote the complexation of the lithium ions at the same time as limiting the formation of ion pairs, which do not contribute to the ionic conductivity.¹¹¹ Solvent characteristics can also be tailored based on whether a linear or cyclic carbonate is used. Cyclic solvents, such as ethylene carbonate and propylene carbonate, are used due to their ability to promote the formation of a stable SEI layer.¹¹¹ They also possess a high molecular polarity, resulting in a greater viscosity. Meanwhile, solvents like dimethyl carbonate and diethyl carbonate give rise to a lower permittivity and viscosity due to their linear structure.¹¹¹ A combination of cyclic and linear solvents at different ratios are often used to achieve optimal solvent characteristics, such as viscosity. The electrolyte additives, such as vinyl chloride are utilised in most solvent systems for LIBs. They generally make up less than 5% (by weight or volume) of the electrolyte and are used for a multitude of tasks including, assisting in the creation of the SEI layer, shielding the cathode from overcharging, reducing gas evolution, improving thermal stability of LiPF₆ and lowering electrolyte flammability.¹¹²

Arguably the most important aspect of the electrolyte to consider is how it decomposes during battery operation as this will have a significant impact on both the kinetic and thermodynamic stability of the battery. The type of decomposition is determined by the electrochemical potentials of the anode and cathode as well as their relation to the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the electrolyte.¹¹³ One form of electrolyte decomposition is beneficial to cell stability as it leads to the formation of the SEI layer. Most electrolytes have a reduction potential around 1.0 V vs Li⁺/Li and an oxidation potential of 4.7 V vs Li⁺/Li, these values denote the outer limits of the electrolyte stability window.¹⁰⁷ The intercalation of lithium into the graphite has a potential between 0 V and 0.25 V; as this is below the reduction potential, outside of the stability window, the electrolyte will decompose at the graphite surface, allowing SEI formation.¹⁰⁷ The SEI itself is formed from the electrolyte decomposition products such as carbonates (Li₂CO₃), oxides (lithium alkyloxide) and active lithium, like lithium fluoride (LiF), from LiPF₆.

The SEI works to counteract many phenomena that would be detrimental to the capacity and lifetime of a battery. For example, while electrolyte decomposition is required to form the SEI, too much decomposition will reduce the capacity and stability of the battery, the passivation of the graphite surface by the SEI will limit further electrolyte decomposition adding additional battery stability.¹¹⁴ Also, SEI formation will suppress another unfavourable process, graphite exfoliation. As an intercalation material, graphite is able to incorporate a wide variety of unwanted guest species into its structure. The most significant of these species are lithium ions encompassed by a solvation shell sourced from the electrolyte. These solvation shells prevent lithium ion pair formation, which usually results in an enhanced electrolyte ionic conductivity. Additionally, the incorporation of solvated lithium ions can greatly expand the graphite matrix, facilitating irreversible structural damage and layer separation.³² A schematic representation of this graphite exfoliation process is given in **Figure 1-12**. When the SEI is present it acts as a

selectively permeable layer on the edges of the graphite, allowing only unsolvated lithium ions to pass through it.³²



Figure 1-12: Schematic diagram showcasing the graphite exfoliation process.³²

The formation of the SEI can also affect the mechanical stability of the anode. The presence of this additional layer adds further compressive stress on the active material. While this compressive stress will be relatively small initially, upon cycling the SEI will become thicker as more electrolyte decomposes, causing the compressive stress applied to the anode to increase. While it has been observed that this added compressive stress enhances the mechanical stability, the SEI becoming thicker and stiffer will lead to it being more susceptible to fracturing, which could lead to additional electrolyte decomposition.¹¹⁵ The SEI can also present some other adverse effects on power density, battery capacity, as well as increasing resistance due to its consumption of the electrolyte.^{112,116} This means that the extent of SEI formation needs to be carefully controlled and explains why parameters such as electrolyte composition and formation cycle conditions are kept confidential by most manufacturers.^{32,116}

1.7 The Faraday Institution and the ReLiB project

Before discussing the main aims of this thesis, it is important to summarise the overall project this investigation is a part of. This work was funded by the Faraday Institution which aims to bring together expertise from universities and industry across the UK to research and develop new electrochemical storage technologies for the

automotive industry. Multiple research strands were established as part of the Faraday institution to tackle the main issues surrounding battery powered EVs.¹¹⁷ One of these research strands was the recycling and reuse project (ReLiB), which this study is a part of. The goals of the ReLiB project include the development of novel and scalable recycling processes, redesigning new batteries with regard to EOL treatments, upcycling of recovered materials and the remanufacturing of new batteries from these reclaimed materials.¹¹⁸ Additionally, LCAs, techno-economic assessments and the proposal of new legislation surrounding LIB recycling in the UK have also been explored in the ReLiB project in order to characterise the environmental, economic and legal challenges that remain with UK LIB recycling. The work shown in this thesis contributes to many of these deliverables such as design for recycling, remanufacturing of EOL materials and environmental assessments.

1.8 Project aims

This investigation aims to explore the role alternative adhesives have on recycling processes and how they can simplify the disassembly of batteries in order to formulate separate, purer waste streams as part of a larger recycling methodology. Initially, this work will focus on the characterisation of anodes formulated using deep eutectic solvent (DES) modified binder materials. Key properties such as adhesion strength, thermal stability, electrochemical performance, and delamination efficiency (in water and mild ultrasound) are compared to anodes made with conventional binders. The base polymers used in these DES-modified systems were water miscible to maintain the processibility benefits of contemporary binders like CMC/SBR. The electrochemical performance of anodes created using graphite recovered from EOL sources, that used ultrasound for delamination, are also characterised in this study. As ultrasound was used as the main methodology for delamination in this work. This was done to further assess the viability of this technique, first established in literature,¹¹⁹ and ensure second-life batteries can attain similar performance to batteries created from pristine active materials. In an effort to enhance other characteristics such as conductivity, conjugated conducting polymers such as PANI were also tested as a modifier for these water miscible binders, by creating polymer blends. The resulting anodes were tested in similar ways to the DES-modified materials, including an assessment of delamination efficiency to ensure any potential improvements to performance do not impede disassembly of these electrodes at the EOL.

The last main goal of this study was to outline how alternative extracellular adhesives can be used, along with design changes, to simplify pack-to-cell disassembly. Example battery packs were created with these alternate designs using a range of different adhesive options before manual and automatic disassembly was attempted and the time and forces required for dismantling were acquired. In order to give some comparison between current commercial battery pack design and these adhesives with that of a Nissan Leaf. This allows comparison between the energy consumption and time taken for dismantling and gives an indication of EOL processing capacity when alternative designs are utilised. A similar environmental impact study was then completed on the delamination steps when using the alternative binders from this study versus PVDF and CMC/SBR to give similar conclusions for cell disassembly.

So, in summary, the main aims of this thesis are:

- Formulate DES-modified binders and incorporate them into anodic materials.
- Fully characterise these materials to compare these systems to conventional binders and determine whether modification has any substantial effects.
- Implement these modified binders into anodes created using recovered graphite from EOL sources and characterise their electrochemical performance.
- Create polymer blends from water miscible binders and PANI.
- Characterise these blends and anode materials made from them to determine whether there are any benefits to other characteristics such as conductivity.
- Manufacture 'dummy' battery packs using a novel pack conformation and alternate extracellular adhesives to show simplified pack-to-cell disassembly.
- Conduct environmental impact studies on pack-to-cell disassembly and delamination of the electrodes after alternative adhesives are incorporated to show the environmental and potential economic benefits of 'design for recycle'.

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Chapter 2: Experimental

2.1 <u>Chemicals</u>

The chemicals used in this project along with their percentage purity and manufacturer are given in **Table 2-1** below.

Name of Chemical	CAS Number	Manufacturer	Purity
Poly(vinylidene fluoride)	24937-79-9	Alfa Aesar	100%
Gelatin (Bovine Skin)	9000-70-8	Sigma Aldrich	100%
Sodium Alginate	9005-38-3	ACROS Organic	100%
Polyaniline	25233-30-1	Sigma Aldrich	98%
Styrene Butadiene Rubber	9003-55-8	Pi-KEM	50% in water sol
Carboxymethyl cellulose	9000-11-7	Acros Organic	99.5%
Choline Chloride	67-48-1	SLS	100%
Glycerol	56-81-5	Fisher	Lab Grade
C-NERGY Spherical Graphite (15 µm)	N/A	Imerys Graphite and Carbon	> 99%
Carbon Black, Super P Conductive	1333-86-4	Alfa Aesar	>99%
Ethylene Carbonate	96-49-1	Sigma Aldrich	99%
Propylene Carbonate	108-32-7	Lancaster Synthesis	99%
Lithium Hexafluorophosphate Electrolyte (LP57)	21324-40-3	Sigma Aldrich	1 M LiPF ₆ in ethyl methyl carbonate:ethylene carbonate (70:30) with 2% vinyl chloride additive
Lithium Metal Discs	7439-93-2	Pi-KEM	>99%

 Table 2-1: Chemicals used during this project, including source and purity.

2.1.1 *Deep eutectic solvent formation*

The deep eutectic solvent (DES) used in this research was a mixture of choline chloride (HOC₂H₄N(CH₃)₃Cl), and glycerol (C₃H₈O₃) in a 1:2 molar ratio, which will henceforth be denoted as ChCl:2Gly. To form the DES the two components were added together in a beaker equipped with a magnetic stirrer bar before being placed upon a hotplate stirrer set at 60 °C. This was then left until a clear, homogeneous liquid was observed. The water content was quantified using Karl Fischer titration to be 0.32 wt % (\pm 0.01).

2.1.2 *DES-modification of gelatin and sodium alginate (Chapter 3)*

The DES-modified gelatin and sodium alginate (NaAlg) binder systems used in this work were created by combining the polymer powders with the DES at different ratios in an agate pestle and mortar. These polymers were mixed together for 10 minutes before they were used to start the manufacturing of the electrode slurry. These modified polymers were made up so the total weight would be approximately 1.5 g and the polymer:DES weight % ratios used for both the gelatin and NaAlg samples were 100:0, 90:10 and 80:20.

2.1.3 Polyaniline polymer blend formation (Chapter 5)

The methodology used to create the polyaniline (PANI) polymer blends was adapted from a paper by Bhadra *et al.*¹ Each composition was made up on a 2 g scale with different samples being made at 10 wt%, 20 wt%, 30 wt% and 40 wt% PANI for each polymer that was investigated. In a beaker the base polymer, either NaAlg or polyethylene glycol (PEG), was mixed with water on a hotplate stirrer until a clear, homogeneous solution, or gel, was formed. The PANI was then added to the beaker and sonicated in an ultrasonic bath (Elma, Fisherbrand FB105055) for 1 hour to ensure good dispersion of the PANI. Once sonicated, the solution was stirred for a further 24 hours on a hotplate stirrer to form a dark green gel-like solution. Films were made up and characterised initially, by casting these solutions onto microscopy slides, which were then dried in in a fanless Genlab Classic Oven (MINO/50) at 40 °C. The compositions which were successfully created and shown to enhance the conductivity were then remade to give the dark green gel-like solution before being implemented into graphite electrodes.

2.2 <u>Electrode manufacturing method</u>

Slurries were made up on a 30 g scale, with a weight % ratio of 90:5:5 with respect to the graphite active material, carbon black and the overall binder system respectively. The polymers used as binders (DES-modified or PANI films) were mixed with water using an overhead stirrer until homogeneous to make the initial binder solution. The carbon black (CB) and the graphite was then added incrementally along with additional water in order to create a thick paste used as the electrode slurry. The slurry was then applied to a 25 μ m copper sheet via a tape casting coater (MTI corporation, MSK-AFA-1) equipped with a doctor blade set at a 100 μ m thickness, at a rate of 7 mm s⁻¹. Once the slurry has been cast onto the copper it is then left in a fanless Genlab Classic Oven (MINO/50) set at 45 °C until the samples were dry.

In chapter 4, an assessment of anode materials manufactured using graphite reclaimed from end-of-life graphite is carried out. In this instance, the same slurry-based manufacturing process was implemented. The recovered graphite was obtained by ultrasonic delamination and the resulting active material was then treated with H_2SO_4 followed by pyrolysis at 500 °C in order to remove any binder residue on the graphite. Blends of pristine:recovered graphite (100:0, 80:20, 50:50, 0:100) were utilised to determine whether the proportion of recovered material used has an impact on the electrochemical performance and morphological structure of the electrodes produced. This anode where this graphite was sourced, was recovered from a dismantled Nissan Leaf battery purchased by the ReLiB project.

The porosity of these graphite electrodes at their initial thickness was then calculated using **Equation 2-1** through to **Equation 2-3**. Porosity gives an indication of the interfacial area between the electrode and electrolyte. Increasing this area will improve the rate capability of the electrode but will negatively influence the mechanical stability.² Porosities of around 40% are usually acceptable for graphite electrodes,³ therefore the thickness that yielded a 40% porosity was calculated and the electrodes were calendered to that thickness using a hot rolling press (MTI Corporation MSK-HRP-1A) set at 6 rpm and 40 °C. It should be noted that the thickness was brought down incrementally and were fed through the rollers 8-10 times forwards and backwards at each increment to ensure a uniform thickness.

$$Theoretical Electrode Density = \frac{1}{\left(\frac{Graphite wt\% \times Graphite Density}{100}\right) + \left(\frac{Binder wt\% \times Binder Density}{100}\right) + \left(\frac{CB wt\% \times CB Density}{100}\right)}$$
(2-1)

True Electrode Density
$$(g/cm^3) = \frac{10,000 \times Electrode \ mass \ (g)}{Electrode \ thickness \ (\mu m)} \times Area \ (cm^2)$$
 (2-2)

$$\% Porosity = \left(1 - \left(\frac{True \ Electrode \ Density}{Theoretical \ Electroide \ Density}\right)\right) \times 100$$
(2-3)

2.3 <u>Microscopy methods</u>

2.3.1 Scanning electron microscopy and energy-dispersive X-rays

Scanning electron microscopy (SEM) is an imaging technique that uses a fine beam of electrons, which are shot at and interact with the atoms located on the specimen surface. Two signals are formed from these interactions, backscattered and secondary electrons, which are used to construct the images. Secondary electron mode was used in these experiments so the morphology of the electrodes can be assessed. The ejection of core electrons by the electron beam will also cause the emission of elemental specific X-rays, which can then be analysed via energy disperse X-ray spectroscopy (EDX) measurements. This allows the chemical composition of a sample to be determined.⁴ The SEM used in this investigation was a FEI Quanta 650 FEG in secondary electron mode, with an Everhart Thornley detector. Images were taken on samples with an area of 1 cm², with a 500x and 5000x magnification and an acceleration voltage of 10 kV. EDX measurements were taken across the same area as the SEM images, over a 10-minute period. The elemental mapping of the surface was carried out and calculated by using the Aztec EDX software. Percentage compositions of the surfaces were attempted but was found to be ineffective due to all the heteroatoms making up the binder having atomic numbers lower than 10, giving rise to peak overlap.⁵

2.3.2 *Atomic force microscopy*

Atomic force microscopy (AFM) was conducted during this study to investigate how different binders may affect the location and distribution of electrode components; a similar technique was used by Terreblanche *et al.* to visualise cathode materials.⁶ The Peak Force Tapping (PFT) mode was utilised to obtain topographical images and estimate Young's modulus values.⁷ PFT involves the oscillation of a cantilever at a frequency lower than that of the resonance frequency, the motion of which, follows a sine wave function. A force setpoint is applied which dictates the contact time between the tip of the cantilever and the sample surface, which generates a force vs time curve. This can subsequently be converted into a force vs. tip-sample separation curve for every pixel of the AFM image. This is then used to determine mechanical properties by looking at the approach and retract curves. In this case the Young's modulus was calculated by using the Sneddon model, which assumes a conical indenter contacting the sample surface and is fitted from the repulsive region of the retract force curve.⁸ The AFM used to obtain images and measurements in this investigation was a Bruker Dimension Icon AFM, Nanoscope V controller and Nanoscope 9.4 imaging software.

2.4 <u>Attenuated total reflectance fourier transform infrared spectroscopy</u>

Attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) is a form of infrared (IR) spectroscopy and is therefore used in the identification of functional groups and bonding present within a particular sample. The basic principles of IR spectroscopy remain the same, IR radiation will only interact with molecules containing a dipole moment which fluctuates during vibrational modes of transport. If the natural frequency of the vibrating molecule, matches that of the incident radiation then IR absorption will occur, causing a reading on the subsequent IR spectra at that particular frequency. Comparing the IR spectra obtained with that present in IR data banks will allow for determination of the functional groups and bonding present within a given sample, additionally frequency shifts and intensity deviations of the absorption bands will indicate changes to the chemical environments surrounding these functional groups.⁹ ATR-FTIR spectroscopy, compared to conventional disperse IR, will analyse a wider range of frequencies, give better signal-to-noise ratios, reduce stray light interference and improve wavenumber accuracy, through the use of fourier transform spectroscopy (FTIR).¹⁰ ATR refers to the technique employed to acquire the IR absorption readings. Figure 2-1 shows how the IR radiation interacts with a sample, essentially an IR light source is applied to the ATR crystal (usually diamond), it is internally reflected at the sample-crystal interface, this will form an evanescent wave, which extends into the sample, the wave will decay exponentially, meaning only the first few microns of a sample is analysed. An absorption spectrum is then constructed from the reflected IR radiation that is recorded by the detector.¹¹



Figure 2-1: A schematic diagram of how infrared radiation passes through an ATR crystal to interact with a sample and provide a subsequent IR spectrum.

This investigation used a Bruker Alpha II ATR-FTIR spectrometer, connected to a computer running OPUS (version 8.1) software to analyse and peak pick the IR spectra that is obtained. For this technique, all synthesised polymer systems were analysed prior to being incorporated into electrode slurries, this is to avoid unwanted impact of carbonaceous materials. Small quantities of the samples were put onto the ATR crystal using a spatula, the clamp was then lowered to ensure good contact and resulting in clear data regardless of the state of the sample. The generated spectra were then peak picked and compared to the data seen in previous studies in order to identify any changes such as new peaks, peak shifts, or intensity changes.

2.5 <u>Thermal analysis methods</u>

2.5.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is used to observe mass changes across a defined temperature range with a specified heating rate. This technique is widely used to conduct polymer decomposition measurements, allowing for a relatively good estimate of substance composition and structure.¹² The apparatus used in this investigation was a Mettler Toledo TGA/DSC1. It possesses a highly sensitive balance and a furnace which provides a resolution of $\pm 1\mu g$ and a maximum temperature of 1100 °C respectively. The machine is also connected to a flow of inert nitrogen gas, which ensures that products of the thermal decompositions are removed from the furnace so they cannot influence the results. The module utilises STARe software (Version 12.10) to record and analyse the resulting spectra. Samples were placed within 100 μ L aluminium pans and weighed before being subjected to a heating program from 25 °C to 500 °C at a heating rate of 5 K/min under a nitrogen flow of 50 mL/min. This program also included a blank curve

subtraction method to counteract the buoyancy effect generated by heating the air inside the furnace. At least three measurements were completed for each sample to allow the error to be determined. TGA was also completed on electrode samples before and after ultrasonic delamination (**see section 2.9**) to determine the amount of residual binder remaining on the recovered active material. This was done by using **Equation 2-4** to calculate the total % binder present before and after processing.

$$Total \% binder in material = \frac{100 \times \% Mass lost in material}{\% Mass lost for lone polymer}$$
(2-4)

2.5.2 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is used to observe how the heat flow changes within a sample pan compared to a reference pan across a linear heating (or cooling) regime.¹³ The sample and reference pans reside on two temperature sensors (thermoelectric disks), and it is through these disks that the heat, originating from a furnace, is supplied to the pans.¹³ DSC has previously been used to identify polymer attributes such as; phase transitions, melting point, crystallisation temperature, glass transitions and even the percentage of crystallinity.^{13,14} Determination of these properties are possible due to the fact that the temperatures of both cells are changed uniformly throughout an experiment. This means that physical transformations (like those mentioned above) will have an impact on the amount of heat required to maintain consistent temperatures between pans.^{13,15} For instance, melting transitions are endothermic, taking in heat to undergo the transition. Therefore, more heating is necessary to ensure both pans stay at the same temperature. Exothermic phase transitions, such as crystallisation will give heat out, meaning less heat is required from the furnace to maintain pan temperatures.¹⁵

The pan temperatures are regulated with a chromel disk and wire that make up the thermoelectric disks. Alumel wires are used to enable individual measurement of each pan so that a thermocouple can determine the temperature difference between the pans due to the heat capacity (C_p) of the sample.¹⁵ Determination of the temperature difference allows the heat flow to be calculated by utilising the thermal Ohm's law equation;

$$q = \frac{\Delta T}{R}$$
(2-5)

Where q is the heat flow of the sample, ΔT is the temperature difference between the sample and reference pans and R is the resistance of the thermoelectric disk.

The DSC used in this investigation is a Mettler Toledo heat flux DSC1, it has an overall temperature range of -150 °C – 500 °C and utilises STARe controlling software (version 12.10). As seen in **Figure 2-2** the furnace will contain a gas, known as the sample gas, which is used to avoid oxidation processes and to allow experiments to be carried out in different atmospheres. Additionally, another gas, called the protective gas, flows around the outside of the furnace to ensure no ice formation occurs during low temperature regimes.¹⁶ For the experiments carried out in this report, nitrogen is used as both the sample and protective gas and was set at a flow rate of 75 mL/min and 150 mL/min respectively. Around 10-20 mg of the samples were placed within 100 μ L Al pans. The pans were then sealed with a lid that has been pierced so that pressure does not build up and to allow gas exchange with the sample gas. The temperature program used heated the sample from 25 °C to 500 °C at a heating rate of 5 K/min. Three measurements were taken for each sample to ensure the consistency of results.



Figure 2-2: Generalized set up of differential scanning calorimetry (DSC).¹⁶

2.6 <u>Physical characterisation methods</u>

2.6.1 Scratch testing

The scratch test is a method of analysing the adhesion capabilities of a material coating a substrate. It involves drawing a spherical, diamond tipped indenter over the sample surface whilst applying a progressive load. The load in which adhesive failure occurs and the coating is detached, revealing the current collector underneath was denoted as the critical load (L_c). This then allowed a quantitative expression of adhesion between the coating and substrate. Afterwards the scratch is analysed using microscopy techniques such as 3D-microscope (3DM) to identify the critical load. It is important to note that this test is comparative, results need to be compared in order to determine how adhesive performance is impacted by the DES content. The machine used in this report was the ST200 scratch tester set with the following parameters:

- Initial Load: 1 N;
- Final Load: 12 N;
- Load rate: 80 N/min;
- Table rate: 200 mm/min.

Samples were adhered onto glass slides using double sided tape before the whole system was clamped onto the machine. Each sample was analysed 3 times, with each scratch being at least 5 mm apart to ensure scratches were not affected by previously failed material (e.g. via crack propagation). The scratches are then imaged at a 5x magnification with a 3DM (Zeta-20 Optical Profiler) and using the Zeta 3D software, multiple images were stitched together in 1 row as to observe the whole scratch in a single image. A digital ruler was then utilised to give the length from the start of the scratch through to the initial delamination in order to obtain the critical load via **Equation 2-6**.

 $L_c = [Load Rate (N/mm) \times Delamination length (mm)] + Intial Load (N)$ (2-6)

2.6.2 Wettability testing

Wetting of electrode surfaces with electrolytes is an important factor when trying to optimise cell performance and limit potential safety risks of the battery. For example, incomplete wetting can lead to irregular charge density distribution, the formation of unstable SEI layers and lithium plating.¹⁷ Additionally, wetting the surfaces with water

should give an idea of how well water interacts with the sample surface and the porosity of the sample, indicating how well delamination may occur in future recycling tests. Wettability was characterised in this report by measuring the contact angle of a drop of solvent on the electrode surface, to determine how well the solvent wets the substrate. Generally, when surface contact angles are $< 90^{\circ}$ they are 'wetting' the surface, whereas angles $> 90^{\circ}$ are 'non-wetting'.¹⁸

Wettability testing was carried out on electrode samples cut to 1 cm² in area and stuck onto a glass slide using double sided tape to ensure the material is as flat as possible. The slides where then placed on a Biolin Scientific Theta Lite One Attension optical tensiometer underneath a syringe filled with the necessary solvent equipped with a square-cut needle. Two solvent systems are utilised in this study, the first one is water and the second is a 'mock' electrolyte solution made up of a 50:50 ratio of ethylene carbonate (EC) and propylene carbonate (PC). A singular drop of liquid was deposited onto the substrate and the live camera recorded the first 20 seconds of contact between the droplet and the substrate while measuring the contact angles. The last recorded contact angle is quoted in this investigation and 3 repeats was taken for each sample, for both water and the mock electrolyte to ensure accurate results.

2.7 <u>Electrochemical testing methods</u>

2.7.1 Coin cell formation

In order to characterise the electrochemical properties of the electrode materials produced during these investigations, coin half cells were manufactured. The electrode samples created previously were into 15 mm diameter discs using an electrode press (MTI Corporation, MSK-T-06) and put into a vacuum oven (Binder, VD056-230V) overnight before being transferred into a glovebox (MBraun, Workstation UNIIab plus/pro - sp/dp). The electrodes were weighed prior to their incorporation into the coin cells. This weight and the theoretical capacity of the graphite (372 mAh.g⁻¹), calculated by **Equation 2-7**, were used to calculate the current rates used during cycling via **Equation 2-8**.

Theoretical Capacity
$$(Ah/g) = \frac{nF}{3600 \times Mr}$$
 (2-7)

 $Current rate (mAh) = Theoretical capacity (mAh/g) \times (Active material \% \times Active layer mass(g))$ (2-8)

Where, n is the number of electrons, F is the Faraday Constant (96,485 C mol⁻¹), Mr is molar mass of active material. As the cells tested in this study were half cells, lithium metal discs were used as the counter electrode. The coin cells were constructed using CR2032 caps and lids, two spacers (1 mm and 0.5 mm width) a wavewasher (15 mm diameter, 1.4 mm width) and a separator between the two electrodes (Cellguard, 19 mm diameter) soaked with 40 μ L of Li57 electrolyte (Sigma Aldrich, 1 M LiPF6, ethyl methyl carbonate : ethylene carbonate (70:30) with 2% vinyl chloride additive). **Figure 2-3** shows how each of the components were added together to construct the coin cells, once created they were crimped with 1000 psi of pressure to ensure good contact between all the components.



Figure 2-3: A schematic diagram showing the different components used in the creation of the coin half cells used in the electrochemical testing of the alternative binder electrode materials and how they were fitted together.

2.7.2 Coin cell cycling

Electrochemical testing of the coin cells was largely carried out via coin cell cycling, were a constant current is applied to the cell across a given potential range to determine key properties such as the capacity of the cell. The current applied, also denoted as the C-rate, is calculated using **Equation 2-8**, where the initial value will correlate to a C-rate of 1 C, which is the current required to charge and discharge the cell within 1 hour. This was then converted to the other C-rates utilised in these experiments by dividing and

multiplying this current value as appropriate, i.e. 0.1 C = 1 C/10. The 3 main experiments used to test these cells were a formation cycle to show initial chemistry such as SEI formation, a rate test to observe the stability of cycling at multiple current rates and long-term cycling to give an indication of how the performance is affected by cell ageing. Due to the fact all cells analysed in this study were half-cells, cycling was conducted between the potentials of 1.5 V and 0.0 V vs. Li/Li⁺. **Table 2-2** gives the full parameters used in each of the experiments, including the C-rates used, the potential range and the number of cycles completed. The coulombic efficiency was also calculated using **Equation 2-9** and was used to confirm SEI formation and the overall efficiency of the cell.

Coulombic Efficiency (%) =
$$\frac{Charge Capacity (mAh/g)}{Discharge Capacity (mAh/g)}$$
(2-9)

Experiment	Potential Range (vs. Li/Li⁺)	C-rates Used	Number of Cycles at Each C-rate
Formation Cycling	1.5 V – 0.0 V	0.1 C	5
Rate Test	1.5 V - 0.0 V	0.1 C, 0.2 C, 0.5 C, 1 C, 5 C, 1 C, 0.1 C	5
Lifetime Testing	$1.5 \ V - 0.0 \ V$	0.1C	50

 Table 2-2: Cell cycling operating parameters for the experiments conducted on all coin cells discussed in this project.

2.7.3 *Electrochemical impedance spectroscopy*

Electrochemical Impedance Spectroscopy (EIS) is a technique used to obtain the electrical impedance of a sample as a function of the frequency of an applied electrical alternating current. EIS works by using a potentiostat to apply a fixed sinusoidal voltage to the coin cells, the voltage will induce a current flow with the magnitude of both the voltage and the corresponding current being characteristic of the system at a given frequency, which allows for the calculation of impedance via **Equation 2-10**.¹⁹ The impedance value gathered from this calculation will have both a real and imaginary component, with the real component being the resistance of the system and the imaginary

component relating to the reactance force, with contributions from both the inductance and capacitance.¹⁹ To get the true impedance from the cell this calculation is completed across a given frequency range, often producing a Nyquist plot.

$$Z_{(j\omega)} = \frac{V_{(j\omega)}}{I_{(j\omega)}}$$
(2-10)

Where, Z is impedance, V is the voltage, I is the current, j is the imaginary component and ω is the frequency.

A Nyquist plot plots imaginary impedance (Z'') against real impedance (Z'). The resulting graph will allow for characterisation of the different contributions to impedance such as charge transfer resistance (R_{CT}), solution resistance (R_S), double layer capacitance (C_{DL}), Warburg element (W) and frequency (ω), **Figure 2-4** shows an example Nyquist plot and associated Randles circuit. This shows how the features of the graph relate to different impedance contributions and how values for these features can be obtained, often via modelling.¹⁹ As seen by **Figure 2-4** these contributors will have an impact on the shape and size of the Nyquist plot, allowing for comparisons between different electrochemical systems. Generally, Nyquist plots with smaller and shallower curves will have a lower impedance than those with larger, wider curves.



Figure 2-4: A generalized Nyquist plot and associated Randles circuit showing contributions from solution and charge transfer resistances, double layer capacitator effects, Warburg element and frequency.

EIS experiments were carried out by using an Ivium nSTAT multichannel potentiostat using the corresponding Ivium software after each cycling experiment detailed in **Table 2-2**. Multiple potentials were tested, which lined up with intercalation

potentials obtained from the formation cycles, these were 1 V, 0.4 V, 0.2 V, 0.15 V and 0.1 V, and all experiments were completed across a frequency range of 300,000 Hz to 0.1 Hz.

2.7.4 Four-point probe conductivity testing

Conductivity testing was utilised in chapter 5 to analyse the conductivity of thin polymeric films. A four-point probe methodology was used, where four probes are present in a line equidistant from each other and are brought into contact with a sample surface. A current is then passed between the outer probes, which causes a change in voltage between the inner probes, which are connected to a voltmeter. Measuring this voltage change allows the sheet resistance (R_{Sh}) to be calculated, allowing calculation of the sample's conductivity.²⁰ For these experiments a Ossila four-point probe was used, along with the associated Ossila sheet resistance software (version 2.0.1.2). **Equation 2-11** shows the calculation used by the software to calculate the sheet resistance, which is then used to calculate resistivity via **Equation 2-12** and finally conductivity via **Equation 2-13**.²⁰

$$R_{Sh} = \frac{\pi}{\ln\left(2\right)} \times \frac{\Delta V}{I} \tag{2-11}$$

$$\rho = R_{Sh} \times t \tag{2-12}$$

$$Conductivity = \frac{1}{\rho}$$
(2-13)

Where, R_{Sh} is the sheet resistance, I is the applied current, ΔV is the change in voltage and ρ is the resistivity.

2.8 <u>Recyclability testing via ultrasonic delamination</u>

An investigation to determine delamination efficiency of anodes created using these alternative binder systems versus conventional binders was done using a novel technique utilising ultrasound similar to that seen in a previous study.²¹ Initial tests involved the use of a low power ultrasonic bath (Elma, Fisherbrand FB105055). In these experiments, samples were cut to 3 cm² and placed within a beaker filled with deionised water. The beaker was then put into the bath, which was set for 5 minutes at room temperature. Once completed, the samples were rinsed with deionised water and left to dry. Images were

then taken to show the effectiveness of the delamination. If samples exhibited low amounts of delamination then the samples were retested using the ultrasonic horn setup detailed in the aforementioned ultrasonic delamination study.²¹ In these experiments, the samples were cut to the same size, and adhered onto a plastic disc (custom made by the University of Leicester Chemistry Workshop) using double sided tape. The plastic disc was adhered to the centre of a crystallising dish using blu-tac and a spirit-level was used to ensure levelness. Then the crystallising dish was adhered to a lab-jack with another piece of blu-tac before the levelness was tested again. An ultrasonic horn (Emerson 20 kHz, 1250 W) was used, and coin cell spacers were implemented to ensure that the distance between the horn and the sample was set at 2 mm, by stacking them onto the sample and adjusting the lab-jack so that the horn was just touching them. The spacers were then removed, and the dish was filled with 75 mL of deionised water. The horn was run for 5 seconds at a set power percentage. Images were taken and compared to show the effectiveness of the delamination using the two ultrasound devices and on electrodes created with different binder systems.

2.9 <u>References</u>

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Chapter 3: Gelatin and alginate binders for simplified battery recycling¹

3.1 Introduction

The current design of lithium-ion batteries (LIBs) makes recycling complex and inefficient compared to lead acid batteries and considerable effort is now being invested in the concept of design for recycle.^{2,3} Recovery of the electrode active materials, such as cobalt, lithium and graphite, is especially important as these are all present on US and EU critical material watch lists.^{4,5} The economics of the recycling process are controlled by the purity of the products and techniques which shred cells are compromised by the low purity 'black mass' produced. A recent techno-economic comparison by Thompson *et al.* indicated that physical separation of the battery components prior to delamination is more profitable than shredding due to the formation of purer waste streams.³ Lei *et al.* proposed a method to separate the active material from the metal foil using high powered ultrasound.⁶ The method breaks the adhesive bond, delaminating an electrode in just a few seconds. However, the process was highly dependent on the binder type present within the electrode. Water dispersible binders would simplify this process and the present study investigates two such binders.

The most common binder used in both LIB cathodes and anodes is polyvinylidene fluoride (PVDF) chosen for its inherent electrochemical stability resulting from its oxidative resistance. It also contributes to a surface passivation layer on the anode that hinders reductive decomposition of the electrolyte and extends battery life.^{7,8} However, the use of PVDF binders exhibits significant limitations when it comes to recycling processes, as PVDF is poorly soluble except in N-methyl-2-pyrrolidone (NMP), which is an expensive and toxic solvent. The chemical stability of PVDF means that high temperature processes are required to decompose the polymer and recover the active material and these result in by-products including HF and CO which must be scrubbed from flue gasses.² Additionally, the production of HF can lead to the fluorination of the oxides within the cathode active materials, which destabilises the lattice structure by dissolving the transition metals. This devalues the cathode materials that would be produced by recycling, so non-fluorinated binders need to be investigated.⁹

Recently alternative binders, such as carboxymethyl cellulose/styrene butadiene (CMC/SBR) and CMC/polyurethane have become more common because CMC is water

dispersible, allowing the replacement of NMP with water during manufacturing.^{10,11} However, the cross-linking of CMC/SBR during manufacturing will limit water solubility for end-of-life processes, so the usage of other water-dispersible binders, which could enable facile separation of active material from the current collector have been investigated. These include guar gum,^{12,13} acrylates,^{13,14} gelatin,^{13,15} sodium alginate^{13,16,17} and chitosan.^{13,18} Use of these can result in production of higher purity waste streams, which will simplify subsequent recycling processes.

Gelatin is one of the most versatile naturally occurring biopolymers and has seen use in several gel-based bioadhesives.¹⁹ This has led to investigations into its use in electrode binders.^{20,21} Gelatin is a heterogeneous mixture of single or multi-stranded polypeptides made up of glycine and proline residues, containing both hydrophilic and hydrophobic groups (**Figure 3-1a**). This amphiphility allows emulsification into water, while being insoluble in organic solvents.¹³ Similarly, alginate-based polymers have also been investigated as bioadhesives and binder materials previously, sodium alginate (NaAlg) can be sourced from brown seaweed and like gelatin is cheaper than PVDF. It is composed of 1,4-linked β -*D*-mannurate and α -*L*-guluronate moieties and possesses a polymer structure capable of extensive hydrogen bonding (**Figure 3-1b**). NaAlg was first studied as a potential binder for Si-based anodes by Kovalenko *et al.*,²² and subsequent studies have demonstrated the effectiveness of NaAlg as a binder for cathode materials such as NMC111 (LiNi_{0.33}Co_{0.33}Mn_{0.33}O₂) and LNMO (LiNi_{0.5}Mn_{1.5}O₄).^{23,24}

Previous work into both gelatin and NaAlg based binders have often discussed their inherent brittleness, with modifiers being used to overcome the problems caused.²⁵ The use of modifiers can also be used to enhance certain characteristics, such as adhesion, flexibility and conductivity.^{26–28} For example, the modification of gelatin with deep eutectic solvents (DESs) increased the elongation of the gelatin materials significantly, 20% elongation with 10 wt% DES increasing to 1200% when 30 wt% DES was added.²⁷ DESs are eutectic mixtures of a quaternary ammonium salt and a hydrogen bond donor, which are held together by ionic interactions to form liquids possessing high viscosities (typically >100 cP or 0.1 Pa.s). They have previously been used in several industries including metallurgy due to their non-volatile nature, the high solubility of metal ions and the greater flexibility in available electrochemistry.^{29,30} Their use as a plasticiser could overcome a key issue surrounding a lack of binder flexibility, hindering volume expansion caused by lithium intercalation, which can cause premature fracturing of the
electrode. Their use as a plasticising modifier to the investigated polymers is done to overcome these issues and to enhance other characteristics.



Figure 3-1: Molecular structures of the gelatin (a), sodium alginate (b) and the DES components, choline chloride (c) and glycerol (d) used in this study.

This chapter will investigate the modification of the gelatin and NaAlg polymers by the DES to identify how the plasticisation of the polymers is occurring based on DES interactions before conducting physical and mechanical characterisation of the graphite electrodes created using these binder systems. 3 different polymer:DES compositions were investigated with the unmodified polymers (100:0) being compared to a small amount of modification (90:10) and a large amount of modification (80:20). Comparisons will be made between the modified and unmodified gelatin and NaAlg systems, as well as with those made with conventional binders, namely PVDF and CMC/SBR. The recyclability will be assessed by investigating the delamination efficiency of the electrodes made using the different binders, using an ultrasound processing methodology outlined by Lei *et al.*⁶ The electrochemical characterisation, including impedance measurements, the solid electrolyte interface layer (SEI), rate testing and lifetime testing are detailed separately in Chapter 4.

3.2 <u>Electrode characterisation and imaging</u>

Anode electrode samples were fabricated from a mixture of the active carbon components, polymer and DES using a slurry and doctor blade methodology described in the experimental section. A range of coated electrodes were prepared so as to compare the morphology and the physical and mechanical performance of the gelatin and alginate binders using different ratios of polymer to DES plasticiser with that of materials created using conventional PVDF and CMC/SBR binders.

3.2.1 Infrared spectroscopy characterisation

Fourier transform infrared spectroscopy (FTIR) was conducted to show the effect of the ChCl:2Gly modification on the chemical shifts of the polymers, which would indicate interactions between the polymer and DES and how increasing the DES content may influence these interactions. The modification of gelatin will be discussed first, the spectra are shown in Figure 3-2, followed by the NaAlg samples in Figure 3-3. The corresponding chemical shifts are detailed in Table 3-1 for all investigated gelatin and NaAlg samples. For both gelatin and NaAlg, the peaks relating to the unmodified polymer absorptions will be assigned, before changes to the spectra as a function of increasing DES content will be discussed, including new peaks and peak shifts. A brief description of the ChCl:2Gly FTIR spectra will be given here to give an idea of the influences the DES will have on the polymer FTIR spectra. The first peak is broad and occurs at 3300 cm⁻¹ characteristic of O-H absorption, partially from moisture content in the DES and partially from the glycerol molecule. The peaks at 2930 cm⁻¹ and 2877 cm⁻¹ are related to the C-H bending vibrations, seen within the ChCl molecule. Additionally, whilst the peaks at 1477 cm⁻¹ and 1415 cm⁻¹ have been credited with the bending of CH₂ due to the similar peaks observed for gelatin, it is important to remember the C-N stretches and additional O-H absorptions that could also be contributing.³¹



Figure 3-2: IR Spectra obtained from the gelatin polymer systems. The samples analysed include unmodified gelatin (100:0) and gelatin modified with ChCl:2Gly at varying compositions; 90:10 and 80:20.

The majority of the structure of gelatin is made up of repeating polypeptide and protein units, which are linked together through the interaction of the amide groups with those on neighbouring polymer chains. As seen in **Table 3-1**, the majority of the IR peaks for gelatin, and subsequently the modified gelatin, relate to numerous amide absorption bands, namely amide-A, amide-B and amides I-III, all of which correspond to the vibrational modes of the peptide bond.³² Unmodified gelatin shows a peak at 3238 cm⁻¹, which is attributed to the O-H absorptions of the hydrogen bonded water molecules and the amide-A absorption band, which relates to the N-H group within the peptide bond. The frequency of this transition is strongly related to the strength of the hydrogen bond it partakes in.³³ The transition at 1622 cm⁻¹ relates to amide-I, which is the C=O stretching and the hydrogen bond couple with COOH groups. The transition at 1518 cm⁻¹ corresponds to the amide-II band, which is the out-of-phase combination of N-H bending and C-N stretching vibrations.^{32,33}

Previous work on gelatin IR characterisation implies that the features observed at 1435 cm⁻¹ and 1383 cm⁻¹ could refer to the symmetric and antisymmetric bending of the methyl groups.³⁴ It is also reasonable that bending vibrations of CH₂ groups could be contributing to the broad 'noisy' peak seen within this IR range. It is important to state, however that within this range there are transitions relating to C-N stretches and additional O-H absorptions that could also be contributing to the noisy broad peak that is

observed at these wavenumbers.³¹ The last main gelatin transition is seen at 1225 cm⁻¹, relating to the amide-III absorption band, which sees the in phase combination of N-H bends and C-N stretches.³³

As the ChCl:2Gly content of the polymer is increased, two observations can be made. Firstly, the DES peaks begin to dominate the spectra, massively increasing the absorbance of the peaks that both components possess. As a result of this, a slight shifting of the peaks to wavenumbers matching that of the ChCl:2Gly reference occurs, which is seen clearly for the CH₂/CH₃ bends and the O-H absorption. The large amount of overlap between the DES and gelatin peaks, as well as the overpowering of the spectra by the ChCl:2Gly absorptions, led to a loss of detail within the FTIR spectra with the peak corresponding to amide-II being observed but peak picking was not possible due to its presence within a noisy portion of the spectra. Secondly, slight blueshifting of the wavenumber for amide bands I-III are seen, with a maximum wavenumber value observed for the 80:20 gelatin:(ChCl:2Gly) composition. These incremental increases in amide I-III wavenumbers were similarly observed in characterisation of gelatin/chitosan composite films were it was determined that these peak shifts were related to the participation of the C=O/COO⁻ groups in the creation of these films via electrostatic interactions.³⁵ A similar mechanism could be occurring here, with the carbonyl groups undergoing an electrostatic interaction with the oppositely charged choline molecule within the DES. This means that the addition of the ChCl:2Gly could be having a substantial effect on the intermolecular bonding interactions between both the neighbouring polymer chains and associated water molecules as the availability of this functional group are integral to the gelatin bonding network and therefore could be implying successful plasticisation of the gelatin.^{36,37}

The FTIR spectra for the unmodified and modified NaAlg binders, shown in **Figure 3-3** with data observed in **Table 3-1**, outlines key functional groups which, were similarly observed in a previous NaAlg characterisation by Hou *et al.*³⁸ Peaks are assigned here primarily using the unmodified spectra, before altercations as a result of DES additions are discussed. The initial peak at 3242 cm⁻¹ is related to O-H stretching of the hydroxyl bonds present on both the NaAlg structure, seen in **Figure 3-1b**, and associated water molecules. The transition seen at 1593 cm⁻¹ corresponds to an asymmetric stretch of the -COO⁻ group, while the set of noisy transitions occurring between 1400-1500 cm⁻¹, with a major peak at 1406 cm⁻¹, relate to various C-H bends upon the polymer backbone. These

transitions are seen throughout all the data, with the main difference being the presence of another peak at approximately 1475 cm⁻¹ once the DES has been added, suggesting it is a CH₂ bend only present in the DES. At 1026 cm⁻¹ there is a C-OH/C-C-O stretch, occurring at a similar wavenumber to the same functional group in ChCl:2Gly. Lastly, a handful of transitions do occur just below 1000 cm⁻¹ but have not been detailed in **Table 3-1** due to no changes being observed regardless of DES content. They are attributed to the uronic acid and mannuronic acid groups, and a lack of variation indicates DES addition makes no significant structural changes to the sodium alginate backbone.



Figure 3-3: IR Spectra obtained from the sodium alginate polymer systems. The samples analysed include unmodified sodium alginate (100:0) and sodium alginate modified with ChCl:2Gly at varying compositions; 90:10 and 80:20.

The FTIR spectra of the modified NaAlg seems to follow a similar trend to that of gelatin, with some of the key functional groups seeing blueshifts in wavenumber as DES content increases. In some cases, like that of the O-H and C-OH/C-C-O stretches, this could be because the ChCl:2Gly is increasing in concentration and 'flooding' the spectra, making the wavenumbers more closely resemble that of the ChCl:2Gly by itself. However, the asymmetric COO⁻ stretch also undergoes a blueshift and is not related to the ChCl:2Gly. In the temperature dependant study that the characterisation is based on, this was also observed as the temperature was increased and indicated a decrease in the hydrogen bonding experienced by the -COO⁻ group.³⁸ It was also determined that the -

COO⁻ group is responsible for the association of hydrogen bonded water, whereas the -OH group takes part in inter/intra chain hydrogen bonding. This, along with the IR data acquired for the ChCl:2Gly-modified NaAlg, implies that the associated water molecules, usually bound to the -COO⁻ group via hydrogen bonding are replaced by the alcohol groups on the glycerol molecule. This could also explain the FTIR data implying a weakening of the hydrogen bonding for the -COO⁻group as these hydrogen bonds are likely to be weaker due to the incoming, larger glycerol molecule relative to water.

From the data and the behaviour of NaAlg in previous studies it is likely that the glycerol hydrogen bonding interactions will be the dominant plasticising effect for the NaAlg samples. However, like with gelatin, there is a possibility for electrostatic interactions, in this case between the choline chloride and the NaAlg, which could be competing or working in tandem with one another. Ideally the two effects will work simultaneously to maximise the plasticising effect. One possible way to determine which mechanism is dominant is by completing the thermal analysis. Based on the paper by Hou *et al.* if the glycerol mechanism is dominant and the -COO⁻ are interacting with glycerol instead of water molecules, the dehydration mechanisms < 100°C would shift to higher temperatures as ChCl:2Gly content increases. However, if the dehydration peaks stay constant, or become broader, it implies glycerol is not replacing the associated water molecules, just becoming associated itself.

Polymer/ChCl:2Gly	Composition	O-H and amide-A	sp ³ C-H Bending	amide-I	Asymmetric COO ⁻	amide-II	Bending of CH2	amide- III	C-OH/C-C-O Stretches
ChCl:2Gly	N/A	3300	2930 2877	-	-	-	1415 1477	-	1035
Gelatin	100:0	3238	-	1622	-	1518	1383 1435	1225	-
	90:10	3273	2937 2876	1635	-	1536	1396 1447	1234	1034
	80:20	3305	2932 2880	1651	-	1542	1411 1476	1236	1039
NaAlg	100:0	3242	-	-	1593	-	1406	-	1026
	90:10	3282	2924 2872	-	1595	-	1404 1476	-	1028
	80:20	3299	2928 2877	-	1600	-	1409 1477	-	1031

 Table 3-1: Table showing the wavenumbers attributed to the key functional group stretches for the unmodified and modified gelatin and NaAlg binders, along with the DES (ChCl:2Gly) as a reference. Stretches shown in red are not applicable to that sample data.

 Functional Group Stretches (cm⁻¹)

3.2.2 Thermal Characterisation

Thermal characterisation of the binder materials was carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), with comparison being made to the key thermal transitions of conventional PVDF and CMC/SBR binders. The binder solutions containing gelatin and NaAlg at each of the ChCl:2Gly compositions were investigated using DSC to observe any changes to the thermal stability of the materials as a function of changing ChCl:2Gly content this is shown in **Figure 3-4** for the gelatin samples and **Figure 3-5** for NaAlg. The binders in isolation were tested here to avoid deviations in the onset temperatures and enthalpy values that would result from the high heat capacity of copper and graphite. TGA was carried out on the electrodes themselves to derive the mass losses attributed to the transitions observed in DSC when implemented into electrode materials. The full thermal characterisation data, including onset temperatures, enthalpy changes, derived from DSC, and mass losses derived from a TGA analysis for each observed transition for every polymer:[ChCl:Gly] ratio is also given in **Table 3-2**.



Figure 3-4: DSC curves showing change in heat flow as a result of the dehydration and melting transitions of the different DES-modified gelatin binders. PVDF and CMC/SBR materials were used as a reference to conventional materials. (exothermic ^)

The thermal stability of gelatin is much lower than that of PVDF and CMC/SBR, with the earliest transition occurring at around 40 °C, relating to a trans-conformation transition, where the gelatin changes from a helical to a coiled configuration.³⁹ This transition occurs within the standard battery operating temperature range (-20 °C to 60 °C) and could lead to significant issues with electrode fracturing and unwanted sidereactions. The close proximity of this initial transition to the glass transition temperature and the melting point of gelatin causes the broad peak observed for all gelatin samples in Figure 3-4. Addition of ChCl:2Gly has a negative impact on the thermal stability, shown by the decreasing onset temperature of this transition as ChCl:2Gly is added. When investigating the thermal properties of gelatin, Michon et al. proposed that association of helical gelatin structures via hydrogen bonding was localised to 'junction zones', which were the first features to be lost upon heating.³⁹ The presence of ChCl:2Gly could limit the formation of these zones, with the additional choline chloride and glycerol molecules hydrogen bonding with the functional groups of the gelatin, acting as a buffer between neighbouring chains, reducing polymer-polymer interactions and the formation of these 'junction zones'.



Figure 3-5: DSC curves showing change in heat flow as a result of the dehydration and melting transitions of the different DES-modified NaAlg binders. PVDF and CMC/SBR materials were used as a reference to conventional materials. (exothermic ^)

NaAlg has a similar broad initial transition to gelatin, which has been attributed to the dehydration and melting of the polymer. However, upon modification with ChCl:2Gly this transition shifts to higher onset temperatures, increasing from 50.85 °C when unmodified, to 78.45 °C in the '80:20' sample. This is of comparable thermal stability to CMC/SBR, which undergoes a melting transition onset at 84.21 °C. The reason behind the shift has been attributed to the water, that is typically hydrogen bonded to the -COO⁻ group of the NaAlg,³⁸ being replaced by glycerol from ChCl:2Gly, due to the similar bonding capabilities between glycerol and water. The fact that this peak is shifting, rather than becoming broader, indicates the replacement of water by glycerol rather than them both being present. This is of particular significance due to the fact that through the modification of NaAlg the thermal stability of the polymer is now outside the LIB operating temperature range and comparable to CMC/SBR. This greatly reduces the risk of electrode degradation and unwanted side reactions that could occur with thermal events occurring within this range.

Determination of thermal stability has focused on the first initial peak observed in the DSC curves on the respective binder solutions. However, thermal characterisation was continued past these values to characterise how these polymers degrade and decompose up to a temperature of 500 °C. Enthalpy values and mass losses were also determined for each thermal transition that is observed, with the full characterisation data being outlined in Table 3-2. For example, it is predicted that even when implemented into electrode materials, gelatin will undergo a supercontraction mechanism consisting of two main endothermic processes; a pre-transitional step (>200°C) where any remaining water is removed and the remaining helical structures degrade, followed by the formation of the coiled macrostructure and the supercontraction of gelatin (>220°C). This two-phase decomposition is observed in Table 3-2 and the associated enthalpy values of -9.98 J g⁻¹ and -54.28 J g⁻¹ seen in the unmodified gelatin are of a similar magnitude to previous studies into gelatin decomposition, which gave 26.77 J g^{-1} and 71.13 J g^{-1} .⁴⁰ In the case of NaAlg this extended thermal characterisation observes the exothermic decomposition of the polymer rather than an endothermic transition, which is seen in gelatin. Previous investigations into NaAlg have noted this two-phase exothermic decomposition process, with an initial decomposition of the NaAlg followed by the formation of a carbonaceous residue and sodium carbonate, with creation of the decomposition products resulting in the exothermic behaviour.⁴¹

Polymer	Composition	Key Thermal Transition	Onset Temperature (°C)	Mass Loss (%)	Enthalpy Change (Jg ⁻¹)
Gelatin	100:0	Melting	44.80 (1.09)	0.094 (0.012)	-194.4 (12.8)
		Polymer Decomposition 1	206.47 (0.55)	0.818 (0.052)*	-9.98 (0.43)
		Polymer Decomposition 2	241.04 (0.95)	0.818 (0.052)*	-54.28 (3.18)
	90:10	Melting	41.30 (0.29)	0.078 (0.002)	-129.5 (11.3)
		DES Decomposition	141.56 (0.49)	0.103 (0.001)	-129.5 (11.3)
		Polymer Decomposition	232.36 (4.43)	0.722 (0.030)	-23.88 (2.11)
	80:20	Melting	39.71 (0.20)	0.074 (0.003)	-183.4 (22.6)
		DES Decomposition	126.37 (10.92)	0.173 (0.011)	-183.4 (22.6)
		Polymer Decomposition	229.66 (2.35)	0.908 (0.067)	-216.2 (16.7)
NaAlg	100:0	Loss of Bound Water/Melting	50.85 (0.89)	0.100 (0.013)	-302.1 (20.4)
		Polymer/DES Decomposition	212.66 (0.09)	0.406 (0.035)	256.7 (27.8)
	90:10	Loss of Bound Water/Melting/DES Decomposition	73.47 (1.08)	0.021 (0.008)	-255.63 (2.19)
		Polymer/DES Decomposition	193.45 (1.05)	0.374 (0.018)	139.37 (6.62)
	80:20	Loss of Bound Water/Melting/DES Decomposition	78.45 (6.85)	0.100 (0.018)	-242.89 (5.95)
		Polymer/DES Decomposition	191.48 (0.12)	0.631 (0.012)	153.86 (9.69)

Table 3-2: Summary of key transitions for every ChCl:2Gly modified gelatin and sodium alginate (NaAlg) composition used. Dehydration and gradual mass loss peaks have been omitted. Errors from standard deviation over three repeats and are shown in brackets and italics.

3.2.3 *Coating morphology*

The electrode morphology was examined using SEM to determine the location of the binder and carbon black (CB) around the larger graphite particles. It was observed that the morphology of both the gelatin and NaAlg electrodes are typical of a graphite anode material made with PVDF, however the gelatin samples exhibit pin-hole defects (**Figure 3-6**). When formed, these pin-holes can propagate via a self-catalytic process, whereby the thermodynamics and kinetics of surface electrochemistry are promoted where the pin-hole defects are located. This localisation and accumulation of surface chemistry at these heterogeneities will lead to additional deformities, further catalysing additional localised reactions and result in premature electrode failure.⁴² The hygroscopic nature of the gelatin⁴³ and the ChCl:2Gly, coupled with the water-based slurry used to create the electrodes, is the source of the pin-hole defects as a relatively large degree of associated water content is present within the initial cast. Upon drying, the expelled water leaves the pits behind.



Figure 3-6: SEM image showing examples of the pin-hole defect present upon the modified gelatin electrode surfaces. Image was acquired using an excitation voltage of 10 kV.

Figure 3-7 shows SEM images of the graphite active material for both the modified gelatin and NaAlg electrodes (images a and b) versus the reference electrodes made with PVDF and CMC/SBR (images c and d respectively). In the gelatin image, the graphite particles are covered in smaller particles, presumably the CB. The coverage of these

particles across the entirety of the graphite, rather than being situated between the particles, is unlike that seen in conventional PVDF and CMC/SBR electrodes, as well as the behaviour observed in the NaAlg image. Typically, a LIB binder will separate into three states during interaction with a surface; bound polymer, where the polymer chemically bonds or adsorbs to the particle surface at bonding sites, immobilised polymer, where the polymer layers of neighbouring particles interact, and free polymer, where polymer is distributed across the active material particles.⁴⁴ PVDF binds to oxygenated hydroxyl and carbonyl groups located on the edge planes of the graphite due its polarity, with immobilised layers existing in the interstitial sites between graphite particles and free polymers being rarely distributed across the entire surface rather than being localised to the edge planes and gaps between the graphite. As gelatin is an amphiphilic polymer, capable of interactions with hydrophilic and hydrophobic materials, it could be interacting with the main body of the graphite, as well as the edge plane, expanding the bound and immobilised polymer layers to the entire electrode surface.



Figure 3-7: SEM images showing surface morphology of graphite bound with a) gelatin and b) sodium alginate both modified 10 wt% [ChCl:2Gly] c) PVDF and d) CMC/SBR. All images were taken using an excitation voltage of 10kV.

On the other hand, the NaAlg electrodes seem to behave similarly to the reference electrodes, with polymeric regions mainly existing towards the edge planes of the graphite and the areas between the graphite particles. As NaAlg is hydrophilic, rather than amphiphilic, it will not bind to the bulk of the graphite particles, instead localising to the edge planes where it is possible to undergo hydrogen bonding with the hydroxyl and carbonyl groups. From there the immobilised phase will form with neighbouring polymeric regions with sporadic distribution of free polymer on the graphite surfaces. **Figure 3-7** shows the morphology of the modified gelatin and NaAlg electrodes with 10 wt% ChCl:2Gly but it should be noted that no difference is observed in electrode morphology or polymer localisation as a function of ChCl:2Gly content.

In order to confirm the observations made in these SEM images, modulus scans using AFM were recorded (Figure 3-8). AFM data were acquired in peak-force mode. Here the AFM scan produces modulus data through the probe coming into contact with the surface until a set point is reached, generating a force-time curve for every pixel on the image. Terreblanche et al. used this technique to identify the different electrode components for NMC cathodes and the same technique and modulus models were used in this study.⁴⁶ It should be noted that the modulus images show a semi-quantitative, comparative contrast in the modulus values; quantitative values for the modulus could not be acquired for these samples. The sample modulus is calculated using tip dimensions, such as the tip radius and tip angle. When the AFM tip is incident on a sample surface these dimensions can change due to deformities and wear. This will therefore affect the calculated modulus values, meaning these values can no longer be taken as 'absolute' values. For the present application, a self-consistent comparative analysis is sufficient to make a distinction between the 'hard' graphite and the 'soft' polymer and CB. Overall, the AFM images support the observations made from the SEM images, reinforcing the proposed differences in how each polymer binds to the graphite active material. The darker areas of the images on the right-hand side correspond to softer regions of the sample, i.e. the polymer and CB. The lighter areas correspond to the harder regions, i.e. the graphite.



Figure 3-8: AFM images for graphite electrodes showing the surface morphology and modulus scans for electrodes used in this study, taken over a 5x5 µm area. The polymers used as the binders included; a) and b) gelatin:(ChCl:2Gly), c) and d) sodium alginate:(ChCl:2Gly), e) and f) PVDF, g) and h) CMC/SBR.

In the case of the gelatin sample, (**Figures 3-8a & b**), the entire sample surface is covered in these darker regions, confirming the presence of a polymer/CB layer. The morphological image in **Figure 3-8a** shows sub- μ m particles in the same area as the 'dark' overlay in the modulus scan, confirming the presence of the CB in these polymeric regions. The presence of this polymer/CB layer across the entire electrode surface could influence both the mechanical and electrochemical behaviour of these electrodes. Firstly, it could strengthen the adhesive bonding, as extra mechanical force may be required to penetrate the surface layer before adhesive bonds between the graphite particles and the copper foil are broken. Secondly, this layer may affect the performance of the battery, as intercalation of the lithium ions may be hindered, or result in changes to the formation of the SEI that is essential for stabilising the anode during cycling.

The NaAlg images (**Figures 3-8c & d**) show a more typical electrode format, where the 'softer' polymeric regions exist on the edges and in between active material particles. The pronounced edges between the two regions showcase the inability of NaAlg to interact with the majority of the graphite particles due to their hydrophobic nature. The lack of resolved CB particles in the morphological image also indicates a weaker interaction between the polymer and the CB compared to gelatin. The reduced interaction with the hydrophobic components may indicate a reduced mechanical strength compared to that of gelatin, with less adhesive interactions that need to be broken and the lack of this layer of polymer and CB on the electrode surface. The AFM images of the PVDF and CMC/SBR reference electrodes (**Figure 3-8e** to **Figure 3-8h**) show similar behaviour to that of NaAlg, reinforcing what was seen with the SEM images emphasising the morphological difference between the hydrophilic (NaAlg and CMC/SBR) and polar materials (PVDF) versus the amphiphilic gelatin as a result of gelatin being able to interact with all electrode components.

SEM and AFM have allowed determination of the polymer location within the electrode systems and have clearly shown the key differences between both polymers based on their natures. Potential issues surrounding the electrochemical and mechanical stabilities of these electrodes have also been outlined based upon location of the polymers and defects found on the electrode surface. Mechanical characteristics of the electrodes as a result of polymer interactions with the active material and surface defects will be discussed in subsequent sections. Additionally, the electrochemical characteristics of the

electrodes created using the modified binders will be discussed in chapter 4 and compared to that of electrodes manufactured with a PVDF binder.

3.2.4 Adhesion testing

Gelatin and NaAlg are both known to be brittle materials, withstanding high loads, but breaking apart without much elongation when sufficient force is exerted. Modification with DESs such as ChCl:2Gly has been effective in improving the degree of elongation in gelatin previously²⁷ and similar modifications have previously been effective at reducing brittleness in NaAlg²⁵ through plasticisation of the polymer chains. A similar effect is in operation here, with the added flexibility of the polymers increasing the total adhesion strength of the materials upon addition of 10 wt % ChCl:2Gly to the binder systems.

The adhesion strength of the electrode to the current collector was determined by the scratch test method. In this case, this involved creating a scratch on the electrode surface with a set starting and ending load. By obtaining the distance from the start point of the scratch to the point where the copper current collector can be observed, the critical load (Lc) applied at this distance can then be calculated using the set load rate (40 N/min) and table speed (200 mm/min). The Lc is a measure of the adhesive bond strength between the active material binder and the current collector, higher magnitudes of Lc correspond to a better adhered, more mechanically stable electrode. **Table 3-3** shows how the adhesive strength of the electrodes created with gelatin and NaAlg changes with ChCl:2Gly content. The most notable aspect is the superior Lc of both gelatin and NaAlg compared to the conventional anode binder materials, PVDF and CMC/SBR. The high adhesive strength of these polymers versus the conventional materials exhibits how electrode performance, as well as end-of-life treatments, could be improved by changing the binders.

 Table 3-3: Scratch test data showing the critical load distribution with changing

 binder-to-ChCl:2Gly content for gelatin and sodium alginate samples. DES-free PVDF

 and CMC/SBR are included as reference points. % difference in critical load for the

 DES modified samples versus the unmodified materials is also given for clarity. Data

 gathered in triplicate, errors in brackets.

Polymer	Critical Load (N)	% Difference in Critical Load
PVDF	3.59 (0.29)	-
CMC/SBR	3.29 (0.10)	-
Gelatin – No ChCl:2Gly	6.39 (0.26)	-
Gelatin – 10 wt% ChCl:2Gly	6.53 (0.09)	+ 2.19 %
Gelatin – 20 wt% ChCl:2Gly	6.24 (0.14)	- 2.35 %
NaAlg – No ChCl:2Gly	4.19 (0.31)	-
NaAlg – 10 wt% ChCl:2Gly	5.68 (0.25)	+ 35.6 %
NaAlg – 20 wt% ChCl:2Gly	2.89 (0.35)	- 31.0 %

Modification of NaAlg has a greater effect on Lc compared to that of gelatin, which suggests that the DES interactions are more extensive with NaAlg. This could be related to the relative size of the molecules and the steric factors that may limit the available sites for polymer-DES interactions to take place, limiting the degree of plasticisation that may occur and subsequently the deviation in flexibility and Lc. However, even with the improvements the ChCl:2Gly makes to the adhesion strength of NaAlg, it still possesses a strength lower than that of all the gelatin electrodes investigated here. This may be related to the extra coating of material across the gelatin electrode surface, which may increase the external forces required to overcome the adhesive inter-graphite and graphite-current collector bonding as this layer needs to be penetrated first. Alternatively, the reduced adhesion strength could be a function of the reduced amount of interactions NaAlg will have with the hydrophobic graphite compared to gelatin, reducing the number of adhesive forces keeping the electrodes together.

3.2.5 *Wettability testing*

The wettability of these electrode materials by water was characterised by measuring the contact angle of water and a 'mock' electrolyte, made up of ethylene and propylene carbonate, in a 1:1 ratio, when incident on the sample surfaces. **Figure 3-9** shows a schematic diagram of the measurement of the contact angle, which can be done in two ways giving an internal or external contact angle. This study will use the internal contact angle from this point on, with the data acquired for each sample being shown in **Table 3-4** for the tests with water and **Table 3-5** for tests completed with the 'mock' electrolyte. Wettability indicates how well a solvent permeates into the electrode material, the tests were used here to indicate whether gelatin and NaAlg still show hydrophilicity after incorporation into these electrodes. Whereas the tests with the 'mock' electrolyte will determine how well electrolyte is taken in by the active material, essential for lithium ion migration during battery cycling and ensuring the battery is as safe as possible.⁴⁷ Both tests are used to measure the feasibility of these electrodes in water-based delamination techniques and coin cell cycling respectively.

During wettability testing materials showing contact angles of less than 90° are considered 'wetted' by the solvent, while those with contact angles greater than 90° are considered 'non-wetted' samples. A reference electrode containing PVDF binder provided a contact angle value of 119.68°, i.e. 'non-wetted', which is expected from the hydrophobic nature of both PVDF and graphite.⁴⁸



Figure 3-9: Schematic diagram showing the difference between the internal and external contact angles.

 Table 3-4: Contact angle values for the modified gelatin and sodium alginate

 electrodes versus the unmodified materials and a PVDF electrode as a reference when

 water is used as the solvent. Data gathered in triplicate, errors in brackets.

Polymer	Contact Angle (°)
PVDF	119.68 (1.29)
Gelatin – No ChCl:2Gly	92.02 (6.57)
Gelatin – 10 wt% ChCl:2Gly	95.50 (4.49)
Gelatin – 20 wt% ChCl:2Gly	110.29 (4.49)
NaAlg – No ChCl:2Gly	68.30 (2.85)
NaAlg - 10 wt% ChCl:2Gly	67.11 (2.78)
NaAlg - 20 wt% ChCl:2Gly	65.88 (3.01)

All of the electrodes containing the gelatin binder show contact angles greater than 90° due to the amphiphilic nature of the polymer paired with the hydrophobic nature of the graphite. As the ChCl:2Gly content increases, so does the contact angle value, potentially due to a decrease in the number of available hydrophilic interaction sites caused by the interaction of gelatin with glycerol. Some limited permeation of water into the electrode is likely, but it is unlikely to be uniform. The limited uptake of water into the gelatin electrodes is predicted to cause issues during the water-based delamination steps discussed in the subsequent recyclability studies, due to the minimal permeability of the water. Alternatively, the binder systems containing NaAlg all have contact angle values of less than 90°, indicating successful surface wetting with water. In these systems, the addition of ChCl:2Gly instead resulted in a slight decrease in the contact angle. While thermal data showed that the addition of DES caused replacement of associated water to bind to, providing a route water can take through the material.

Wettability testing data for these electrodes using the 'mock' electrolyte is detailed in **Table 3-5**, unlike the testing with water none of the contact angle values surpass 90°, with the PVDF contact angle of 14.89° correlating with previous electrolyte wettability studies on conventional anode materials.⁴⁹ Contact angle values $< 90^{\circ}$ indicates successful wetting of all the electrodes, which is imperative for stable SEI layer formation and avoiding electrochemistry localisation during battery cycling. This should avoid the negative impacts relating to poor electrode wetting, including poor battery performance and lithium metal dendrite growth, which presents severe safety issues.⁴⁷

The NaAlg samples are also shown to possess similar wettability to the PVDF samples, presumably this is related to the morphology of the PVDF and NaAlg electrodes being similar, due to the edge plane localisation of the binder and CB regions as seen in SEM and AFM. The morphology of the gelatin electrodes in relation to the PVDF and NaAlg samples is predicted to be the reason for the elevated contact angle values. As the polymeric and CB region covers the majority of the electrode surface, rather than being localised, this may impede the permeation of the electrolyte through the material, resulting in the higher contact angle. While it is unclear without electrochemical data, which will be discussed in chapter 4, the reduction in electrolyte permeability could imply that the gelatin electrodes may be more unstable and have a lower capacity retention than the NaAlg electrodes.

 Table 3-5: Contact angle values for the modified gelatin and sodium alginate

 electrodes versus the unmodified materials and a PVDF electrode as a reference when

 a 1:1 ethylene carbonate and propylene carbonate solution is used as the solvent.

 Data gathered in triplicate, errors in brackets.

Polymer	Contact Angle (°)
PVDF	14.89 (0.25)
Gelatin – No ChCl:2Gly	45.98 (2.45)
Gelatin – 10 wt% ChCl:2Gly	42.51 (0.99)
Gelatin – 20 wt% ChCl:2Gly	37.80 (0.13)
NaAlg – No ChCl:2Gly	11.08 (3.26)
NaAlg – 10 wt% ChCl:2Gly	20.36 (0.52)
NaAlg – 20 wt% ChCl:2Gly	20.55 (0.73)

The presence of the ChCl:2Gly, similar to the contact angles when using water as the solvent, has an opposing effect for each polymer. For the gelatin materials there is an incremental decrease in the contact angle (increasing wetting) with ChCl:2Gly content, whereas for NaAlg the contact angle doubles upon addition of ChCl:2Gly before stabilising just above 20°. For the gelatin material, the presence of ChCl:2Gly could be working to destabilise the polymeric/CB coverage due to a reduction in polymer-polymer interactions or the hygroscopic nature of the ChCl:2Gly influencing the permeability of the electrolyte through this region. At this point it is unclear what is causing the increase in contact angle for the NaAlg materials, but due to the close proximity to the PVDF wettability in previous studies it is predicted that this will have negligible impact to battery performance and safety.

Overall, the wettability data indicates that while the NaAlg interacts with and takes on water relatively easily compared to gelatin, both materials are wetted by the 'mock' electrolyte. These results indicate that the NaAlg electrodes will have sufficient interactions with the electrolyte, and consequently the lithium, during battery cycling and with water during end-of-life delamination processes. This implies that the mechanical and morphological characteristics of the NaAlg cells will not impede cycling and will interact and delaminate successfully in water. The gelatin materials also show acceptable wetting with electrolyte, implying they can reversibly intercalate lithium, however the polymeric covering of the active material could impede this, as well as interactions with water during delamination studies.

3.2.6 *Recyclability studies using ultrasound*

Ultrasound techniques were employed to show the efficiency of electrode delamination when these novel binders are utilised. The electrodes were submerged in deionised water to observe whether the use of water soluble binders does facilitate recycling processes and limit the need for harsher, more expensive solvents or additives, which are required for some commercial materials.⁶ Due to the water soluble nature of these polymers and the effectiveness of this method on CMC/SBR electrodes previously,⁶ a low powered ultrasonic bath system was tested first to show how further improvements to the ultrasound separation could be made by using these binders. **Figure 3-10a** to **Figure 3-10d** shows the electrodes before and after processing in the ultrasonic bath to show the degree of delamination the procedure incurs. Even though both polymers are

water soluble they behave differently. The material using the NaAlg binders almost fully delaminated within the first 10 seconds of sonication. On the other hand, the gelatin electrodes retain the majority of the active material after processing with the ultrasonic bath.

For the NaAlg materials it is predicted that the water is sufficient to break the majority of the adhesive bonds, with the ultrasound acting as a catalyst to improve the rate of separation. Whereas for the gelatin samples, the amphiphilic nature of gelatin means that water does not interact as extensively as hydrophilic materials limiting the ability to associate with bulk water to disrupt adhesive bonding. However, as seen in Figure 3-10b some defects such as cracking and pin-hole defects are formed during the ultrasonication process, which shows that ultrasound affects the cohesiveness of the active material. This implies that high powered ultrasound, similar to that used by Lei et al,⁶ may be sufficient to fully delaminate the gelatin electrode material. Figure 3-10e and Figure 3-10f show the images of these electrodes, made with gelatin binders, before and after high intensity ultrasound processing. Unlike the commercial electrodes discussed in the ultrasonication study, a power output of only 10% operated for 5 seconds was sufficient to delaminate the active material from directly underneath the sonotrode, as well as inducing more extensive cracking of the electrode in the surrounding area. It is thought that by utilising a continuous flow process, full delamination of the gelatin electrodes can be achieved using high powered ultrasound on a 10% power setting, without the use of expensive solvents or additives as water is sufficient to delaminate these materials.



Figure 3-10: Images showing electrodes before and after processing with different ultrasonication techniques. An ultrasonic bath (power intensity $\approx 0.02 \text{ W cm}^{-2}$) at room temperature for 5 minutes is used in images a) to d). Images a) and b) are the gelatin electrode, and images c) and d) are the sodium alginate electrode. Images e) and f) show the effect of a high-powered ultrasonic horn (power intensity $\approx 398 \text{ W cm}^{-2}$) on the gelatin electrodes at 10% power for 5 seconds.

It is clear from these recyclability studies that electrodes manufactured using these alternative binders can be delaminated efficiently with minimal power input, utilising only water as the solvent. Whilst the nature of the gelatin requires harsher conditions, compared to the NaAlg samples, the power requirements and removal of any additives required to delaminate these electrodes still presents potential environmental and economic benefits. Both in terms of manufacturing and recycling processes, removing harmful solvents, using cheaper materials and reducing the power and time requirements to treat battery materials. Additionally, analysis of the resulting graphite material was conducted to determine the amount of binder residue that remained after delamination, compared to a CMC/SBR reference. For this experiment NaAlg was tested against CMC/SBR using the ultrasonic bath described above. NaAlg was the only one tested in this experiment due to the limited amount of anode material recovered from the gelatin samples from the poorer delamination. Also, from the characterisation shown in this work, NaAlg is a more viable binder replacement to CMC/SBR, compared to gelatin. **Table 3-6** shows the total weight percentage of the binder within graphite active materials before and after ultrasonic delamination in water measured by TGA.

 Table 3-6: Values for the percentage binder within anode materials created using

 CMC/SBR and NaAlg binders before and after ultrasound delamination. Data was

 obtained via thermogravimetric analysis.

Anode Binder	Calculated % Binder Before	Calculated % Binder After
CMC/SBR	4.27 (0.17)	3.95 (0.07)
NaAlg	6.30 (0.42)	1.50 (0.03)

The data shows little deviation in the CMC/SBR data before and after ultrasound giving a relatively small mass loss of 7.5%, indicating most of the polymer remains adhered to the graphite. Meanwhile the NaAlg electrodes showed a 76% mass loss, implying that the majority of the polymer is solubilised during delamination. While this is not a complete loss of polymer it is still significant as this could remove the need for high temperature processing post-ultrasound. It is thought that the reason CMC/SBR does not get removed during water-based ultrasonic delamination is because it undergoes cross-linking with graphite during manufacturing, limiting the solubility in water and

leaving polymer residues upon the graphite. This residue is only fully removed with thermal treatments. As the NaAlg binder is mostly removed during delamination it will limit the need for subsequent thermal treatments to eliminate binder contamination, which will reduce the environmental and economic burden of the overall recycling procedure.

3.3 <u>Conclusions</u>

This work demonstrates the creation of DES-modified gelatin and NaAlg binders, which were successfully used to make anodic coatings on copper foil. Despite the similarity of the two polymers, their inherent properties and, in some cases, the effect of the ChCl:2Gly on these properties would differ. For instance, the morphological imaging of these electrode coatings found that the gelatin binder formed a polymeric layer across the surface of the electrode, whereas the NaAlg binder behaved in a similar manner to PVDF, in that it was located in discrete locations around the edges of the graphite particles. Additionally, FTIR testing found that the interaction of the ChCl:2Gly was different for each polymer. The NaAlg system underwent hydrogen bonding with the glycerol from the DES, also replacing associated water with the DES system, whilst the gelatin electrostatically interacts with the DES to the binder system.

Mechanical characterisation of these electrodes found the plasticising effect of ChCl:2Gly on gelatin and NaAlg resulted in a higher adhesive strength of the material versus electrodes made with PVDF and CMC/SBR binders. However, only the modified NaAlg system showed thermal stability comparable to the CMC/SBR system, as thermal degradation of gelatin took place within the normal operating range of a LIB. Most importantly for this project is the impact these novel binder systems have on the recyclability of the electrodes. These studies were done by observing the degree of delamination of the gelatin and NaAlg coatings using an ultrasonic water bath and, in the case of gelatin, high-power ultrasound set at 10% power. Both samples showed improved delamination versus PVDF in literature, exhibiting how changing the binder within LIBs can have a profound effect on the separation of the active material and current collector, reducing energy requirements and the need for expensive and potentially harmful solvents and additives. Additionally, it was shown that the amount of residue binder adhered to the recovered graphite was minimised when a NaAlg binder was used versus CMC/SBR. Removal of binder contamination will further purify the resulting waste streams after

delamination reducing the number of processing steps post delamination. Due to these properties, these binders show promise in LIB applications, especially with regards to designing electrodes for ease of separation. However, the electrochemical performance of anodes created using these binders must be characterised before a full conclusion can be made. This electrochemical characterisation will be the subject of the next chapter.

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Chapter 4: The effect of using alternative binders and second life graphite materials on the electrochemical performance of lithium-ion battery electrodes

4.1 Introduction

The previous chapter outlined extensive characterisation of the anode materials produced using graphite as the active material along with deep eutectic solvent (DES) modified gelatin and sodium alginate (NaAlg) binders. That work showed that the DES influenced the thermal stability and adhesive strength of the resulting anodes whilst also exhibiting high delamination efficiency under mild conditions. However, a discussion about the electrochemical characteristics of these anodes was not made and instead will be discussed in this chapter. Electrochemical characterisation via coin cell cycling is an essential aspect of analysing the potential performance and stability of novel electrode materials.^{1,2} In the case of the DES-modified binders, analysis of the long-term stability is particularly important due to some of the features discussed in the previous chapter. Including structural defects, observed on some of the electrode surfaces and other structural changes seen in the gelatin materials, which are not observed in the anodes using commercial binders and NaAlg, i.e. the additional carbon black/polymer coating seen upon the graphite particles in the gelatin samples.³ These heterogeneities and the potential for other side reactions based on the functional groups of the polymers, notably the -OH groups, capable of interacting with the lithium ions responsible for charge/discharge present possible capacity fading and impedance rise mechanisms that could affect cell performance and long-term stability. Therefore, an assessment of the electrochemical characteristics of these electrode materials is necessary to determine the true viability of these alternative binder systems so the aforementioned recyclability and adhesive benefits discussed in previous work can also be exploited.

Following on from this work, the assessment of anode materials using end-of-life commercial graphite, reclaimed using ultrasonic delamination, was also carried out. This is an essential aspect in determining the success of a recycling procedure with regards to a circular economy, as the active material performance after recovery needs to be as close as possible, if not identical, to that of pristine active materials. Therefore, as well as discussing the electrochemical properties of anodes using DES-modified binders, the electrochemical performance of electrodes manufactured with pristine and reclaimed graphite is presented and compared to electrodes formulated using two common commercial binders, PVDF and CMC/SBR. The formation of the SEI layer was investigated via coin cell cycling and impedance spectroscopy. Lifetime testing of the half cells was carried out where it was seen that the NaAlg cells exhibited the highest capacity retention. The presence of reclaimed graphite in the anode materials resulted in decreased capacity and Coulombic efficiency, most likely due to morphological changes to the graphite caused by the ultrasonic reclamation process.

4.2 <u>Electrochemical cycling of anodes using DES-modified binders</u>

4.2.1 Formation cycling

The formation of the solid electrolyte interphase (SEI) is an essential component of battery manufacturing, where electrons from the electrode surface interact with the electrolyte, resulting in a reductive decomposition of the electrolyte species. At low potentials, these decomposition products, such as lithium carbonate, lithium ethylene dicarbonate and lithium fluoride, will precipitate onto the electrode surface and form the SEI layer.⁴⁻⁶ The quality and thickness of the SEI layer that forms impacts the performance and longevity of the battery, by limiting interaction between electrons from the electrode and the electrolyte, minimising further electrolyte decomposition, and improving Coulombic efficiency of the battery. While this process has been thoroughly characterised for electrodes using the common commercial binders, it is critical to investigate whether the use of the DES-modified binders impacts on the crucial SEI formation processes that occur during the initial charge and discharge cycles. A relatively low C-rate of 0.1C was used for these formation cycles in order to establish a SEI layer with sufficient coverage across the entire anodic surface. The average capacities and Coulombic efficiencies for half cells with the different binder systems investigated are presented in Table 4-1. While comparing half-cell capacities provides an indication of cell performance at this C-rate, the change in Coulombic efficiency when comparing cycle 1 and cycle 5 provides evidence of SEI formation. This is because Coulombic efficiency is related to irreversible capacity loss, which in these systems is related to the proportion of lithium ions that interact with the electrode during charging, but are not released when the electrode is discharged.⁴

All of the half cells for the binder systems investigated display a Coulombic efficiency during cycle 5 of ca. 96 to 98 %, which is lower than the ca. 99 % efficiency usually quoted for conventional cells. Given that all of the binder systems, including the PVDF and CMC/SBR, show the same behaviour, it is thought that this may be related to additional electrolyte decomposition and SEI growth occurring, as numerous formation cycles may be required before high (> 99%) efficiencies are achieved.^{7,8} The charging and discharging capacities on the 5th cycle were similar for all systems, at an average capacity of 300-335 mAh.g⁻¹, which is comparable to literature values for graphite halfcells, where the initial cycling data are often close to the theoretical capacity of graphite (300 mAh.g⁻¹ to 400 mAh.g⁻¹).^{9,10} The data in **Table 4-1** show some variation in capacity, notably gelatin 80 cells show elevated capacity of 333 mAh.g⁻¹, while gelatin 90 and NaAlg 80 show slightly reduced capacities during cycle 5 of 300 mAh.g⁻¹ and 306 mAh.g⁻¹, respectively. As these capacity variations are relatively small, the changes in environmental conditions during cycling between different measurements and laboratories may be the cause. However, future experiments utilising in-situ techniques, such as Raman spectroscopy, may determine whether or not the DES or the binder have a direct impact in the electrochemistry of the cells. This may account for some of the capacity variation.

Binder	Cycle Number	Average Charge	Average Discharge Capacity	Average Coulombic Efficiency
		Capacity (mAn.g ⁻)	(mAn.g ⁻)	(70)
PVDF	1	295 (25)	251 (20)	85.5 (1.1)
	5	315 (9)	305 (1)	96.6 (1.6)
CMC/SBR	1	294 (27)	263 (21)	86.6 (1.2)
	5	312 (3)	301 (6)	95.9 (2.6)
Gelatin 100	1	308 (24)	278 (10)	89.1 (2.1)
(Gelatin:DES 100:0)	5	319 (18)	307 (12)	96.3 (0.9)
Gelatin 90	1	285 (10)	267 (10)	90.9 (0.9)
(Gelatin:DES 90:10)	5	300 (8)	292 (13)	97.5 (1.4)
Gelatin 80	1	311 (11)	287 (11)	88.9 (1.1)
(Gelatin:DES 80:20)	5	333 (11)	326 (12)	97.9 (0.5)
NaAlg 100	1	320 (20)	284 (17)	88.8 (0.2)
(NaAlg:DES 100:0)	5	315 (8)	307 (11)	97.2 (1.0)
NaAlg 90	1	319 (11)	285 (25)	86.3 (3.1)
(NaAlg:DES 90:10)	5	321 (10)	307 (7)	95.9 (1.1)
NaAlg 80	1	303 (19)	278 (26)	88.6 (1.6)
(NaAlg:DES 80:20)	5	306 (11)	293 (5)	97.6 (0.8)

Table 4-1: Formation cycling data for all polymer systems investigated in this study. Charge and discharge capacities were obtained by taking an average of multiple coin cells, the standard deviation given in brackets. 'Charge' refers to the movement of lithium into the graphite.
Voltage profiles are also shown here to determine whether there is any indication of changes to the lithium intercalation mechanism. Lithium intercalation into graphite is a multistep process, as shown by the anodic half-cell voltage profile in **Figure 4-1**. Each inflection in the voltage profile correlates to a different stage of lithium intercalation, and each stage is illustrated by a schematic diagram. The stages of intercalation have been investigated in previous studies, where lithium insertion and rearrangement of the graphite layers occurs at voltages below 0.25 V in order to achieve the optimal stoichiometry of LiC₆ necessary to maximise lithium content and achieve a capacity close to the theoretical capacity of graphite (372 mAh.g⁻¹).^{11–13} The voltage charge and discharge profiles for the 1st and 5th cycles of the coin cells analysed in this study are presented in **Figure 4-2** and **Figure A1**. The general appearance of the curves and the potentials in which the plateaus occur indicates that lithium intercalation proceeds via the same mechanism regardless of the binder used. The fact that the use of the alternative binders does not alter the lithium intercalation procedure is thought to be the reason behind the comparable capacities for all coin cells made with the different binders.



Figure 4-1: NaAlg cell voltage profile with annotations showing the features that relate to the stages of lithium intercalation; 1L, 4, 3, 2L, 2, 1 with schematic representations. Where the number refers to the number of graphene layers between layers of lithium and the 'L' term indicates stages where lithium is not perfectly ordered and behaves in a liquid-like manner.^{11,12,14}

It should be noted that in most of the voltage profiles for cycle 1 shown in Figure 4-2 there is also a feature just below 0.7 V (0.8 V for CMC/SBR cells), identified by the 'ED' annotation. This is thought to be related to the decomposition of the carbonate-based electrolyte in order to form the bulk of the SEI layer.¹⁵ While this feature is absent in the gelatin binder voltage profile (Figure 4-2c), the rise in Coulombic efficiency from cycle 1 to cycle 5 shown in Table 4-1, and the other voltage profiles relating to gelatin binders in Figure A1 provides evidence electrolyte decomposition and SEI formation is proceeding. However, previous visualisation of the electrodes via SEM and atomic force microscopy showed that when gelatin was used as a binder, the graphite particles were coated with a layer of carbon black and gelatin, rather than the binder being distributed between the graphitic particles. This effect was considered to be due to the amphiphilic nature of gelatin, allowing interaction with the entirety of the graphite surface, rather than solely interacting with the edge planes of the graphite like the other polymers (PVDF, CMC/SBR and NaAlg).³ This study theorised that this layer may be capable of impeding ion movement and contributing more impedance to the cells using gelatin, diminishing the electrochemical performance. While no significant change in capacity or Coulombic efficiency is observed in the formation cycles further testing, notably EIS, may show the effect of this alternative polymer behaviour.



Figure 4-2: Voltage profiles of the 1st and 5th cycles (0.1 C) for each of the Li-graphite half-cells investigated in this study with different binders. Solid lines are the 'charging' curves and the dashed lines are the 'discharging' curves. a) PVDF, b) CMC/SBR, c) gelatin 90, and d) NaAlg 90.

Ultimately, however, the formation cycling data depicted in this section show that the choice of binder has not affected formation cycling performance. The Coulombic efficiency data indicate that SEI formation proceeds at a similar rate regardless of the binder used and the capacity performance has been shown to be relatively unaffected by the type of binder used. While the presence of DES as a plasticiser seems to have minimal impact on the performance of these cells, in-situ analysis, such as Raman spectroscopy, should be carried out in future work to guarantee that the capacity variation between samples is brought about purely by external factors.

4.2.2 *Rate and lifetime testing*

Further testing of these cells to characterise performance retention based on the C-rate and cell ageing was conducted to ensure that the use of the modified binders would not limit the lifetime or potential high-rate applications of these batteries versus the conventional binders. **Figure 4-3** shows waterfall plots taken for a selection of the binder systems analysed in this study, comparing the capacity changes for cells made using the DES-modified gelatin and NaAlg samples with cells made using the commercial binders. The same compositions shown in **Figure 4-2** are used in this figure, with the remaining waterfall plots showing the other DES compositions given in **Figure A2**. For all the anodes tested in these experiments the capacity when using a cycling rate of 5 C was the same (~ 17 mAh.g⁻¹), it is therefore assumed that this is a limitation of the graphite active material. This limitation is not thought to be structural damage, as all cells show a regeneration of capacity when being cycled at 0.1 C again after cycling at higher cycling rates. Rate capability limitations of graphite are well documented above charging rates of 1 C, although the reasons behind the poor performance at these rates are not entirely understood.^{11,16} However, it is thought that a variety of contributions are causing the phenomena, including morphology,^{17,18} SEI chemistry,¹⁹ temperature,²⁰ desolvation of lithium during initial intercalation step,^{19,21} and poor diffusion within the experimental timescale during faster cycling.²²

During these experiments, the majority of these factors should remain the same regardless of the binder used. Notable exceptions are the morphology of the gelatin anodes, due to the presence of the polymeric layer coating the active materials, and the temperature, which was not able to be controlled during these experiments and could impact cell capacity. However, it is the former effect that is the most detrimental to cell performance. The anodes using gelatin binders show a noticeable reduction in rate capability compared to when the other binders are used, where the 1 C capacity for gelatin samples is similar to that registered at 5 C (~ 20 mAh.g⁻¹). While anodes made with the other binders do show reductions in capacity at 1 C, they all still possess capacities $> 100 \text{ mAh.g}^{-1}$. As gelatin samples were the only ones to show this behaviour in these experiments it is thought that the limited performance is a result of the polymeric/carbon black coating on the graphite particles. Additionally, during long term cycling experiments, data given in Table 4-2, cells using gelatin binders exhibited significant capacity reduction (20-40% loss) after 20 cycles at 0.1 C, so even at low cycling rates, electrochemical stability of these cells is severely limited. It is predicted that the presence of this extra polymeric coating will increase the surface area of these electrodes at the electrodeelectrolyte interface, instigating additional electrolyte decomposition and SEI growth compared to the other samples.⁴ Subsequently, it is thought that this will cause greater cell impedance, both from SEI and the polymeric coating itself, and an increased amount of active

lithium lost to the SEI layer. Both of which would lead to minimised lithium intercalation and cell capacity.



Figure 4-3: Waterfall plots showing how the C-rate applied to the half-cells affects the capacity (mAh.g⁻¹). Black symbols show graphite charging, red outlines show graphite discharging. a) PVDF, b) CMC/SBR, c) gelatin 90, and d) NaAlg 90.

The similarity in polymer location and binding mechanisms for NaAlg, PVDF, and CMC/SBR results in similar capacity and electrochemical behaviour for the different cells at the different cycling rates.³ The waterfall plots for the PVDF (**Figure 4-3a**) and unmodified NaAlg (**Figure A2c**) anodes are almost identical, showing that the electrochemical stability and performance of these different binder materials are comparable. Upon addition of DES, as seen in **Figure 4-3d** and **Figure A2d**, this performance is further increased at 1 C, where the capacities are ~ 70 mAh.g⁻¹ greater than when no DES is present. The DES used in this investigation, ChCI:2Gly, has been shown to replace the associated water content of NaAlg systems with the glycerol component of the DES.³ The addition of glycerol additives into anode binders have been explored previously, and have been shown to improve the rate capability of

graphite anodes by improving lithium ion diffusion across the anodic interfacial region through improvements to interchain free volume and dielectric constant.²³ It is therefore reasonable to assume that a similar effect is happening here when ChCl:2Gly is present. Other studies into the dielectric properties of ChCl:2Gly compared to glycerol indicate that dielectric behaviour could be further enhanced with the ChCl present, but this improvement was observed in the liquid DES and it is unclear whether this improvement would also be observed when ChCl:2Gly is used as a binder additive. Long-term cycling of the NaAlg cells also showed better performance than the gelatin systems, with only a 5-8% capacity loss over the first 20 cycles compared to the 20-40% loss seen for gelatin. The long-term cycling performance of anodes using NaAlg is also consistent with the reference anodes using CMC/SBR, also shown in **Figure 4-2**. This capacity retention is also similar to that seen for commercial cell materials seen in previous studies, regardless of the DES content used, strengthening the possibility for the use of DES-modified NaAlg as a binder material in commercial LIBs, especially when the enhanced recyclability characteristics are considered.

From the data obtained, it is clear that gelatin-based binders present limitations towards the electrochemical performance of the anodes, as a result of how the binder binds to the graphite particles. Meanwhile, NaAlg-based systems show similar cycling characteristics to cells made from commercial PVDF and CMC/SBR binders, with the addition of DES enhancing the rate capability of the anodes using NaAlg created in this study. Therefore, a NaAlg-based binder was used in the subsequent experiments investigating anodes created from reclaimed graphite active materials.

Binder System	Capacity Retention (%) at Cycle 5	Capacity Retention (%) at Cycle 10	Capacity Retention (%) at Cycle 20	Capacity Retention (%) at Cycle 50
CMC/SBR	97.3 (0.4)	90.9 (1.7)	88.9 (4.7)	81.9 (3.2)
Gelatin 100	94.1 (0.8)	85.7 (0.5)	61.1 (8.9)	32.1 (3.0)
Gelatin 90	95.8 (2.0)	91.0 (4.3)	77.7 (7.3)	35.8 (4.9)
Gelatin 80	94.3 (0.3)	86.7 (1.3)	60.6 (0.7)	32.9 (5.1)
NaAlg 100	98.6 (0.4)	96.9 (0.7)	92.2 (3.1)	84.1 (3.8)
NaAlg 90	99.3 (0.2)	98.2 (0.9)	95.4 (1.9)	81.6 (1.4)
NaAlg 80	98.9 (0.5)	98.0 (1.2)	92.9 (3.4)	84.7 (6.2)

Table 4-2: Capacity retention data (%) for anodes using DES-modified binders across the course of 20 cycles at a C-rate of 0.1 C. These samples are compared to CMC/SBR reference cells.

4.3 Electrochemical cycling of anodes using reclaimed graphite

One of the major barriers to the reuse of graphite reclaimed from production scrap or end-of-life batteries is the presence of the original binder. This affects how the graphite can be separated from the copper current collector, and whether any additional binder removal steps are required. For example, CMC/SBR binders undergo cross linking, limiting the solubility in water which could lead to the majority of the binder remaining adhered to graphite after recycling procedures depending on water solubility.²⁴ A thermal or solvent treatment will therefore be required in order to remove residual polymer from the reclaimed active material.

To quantify the amount of binder remaining on the reclaimed material after delamination, thermogravimetric analysis was carried out on electrodes before and after ultrasonic delamination in water. **Equation 2-4** was used to calculate the total % binder within the electrodes in order to determine how much had been lost from ultrasonic processing. The sample containing CMC/SBR as a binder shows a mass loss of only 7.5% after application of ultrasound, confirming that most of the polymer remains adhered to the graphite. On the other hand, the electrodes containing NaAlg as a binder showed a 76% mass loss, implying that the majority of the polymer is removed during ultrasonic delamination for 5 seconds. While removal of the binder is still incomplete during the short delamination step, a supplementary water washing step could be introduced to complete the removal process. The benefit of using this water-soluble binder is that high temperature processing of the reclaimed post-ultrasound

is no longer required, decreasing both the cost and environmental impact associated with recycling of the electrode materials for second-life applications.²⁵

The second major barrier to reuse of reclaimed graphite is whether the recovery methods have damaged the integrity of the graphite particles by causing fractures within the particles, shearing layers off, or by shattering them completely. Any damage or size reduction to the particles will result in a greater surface area for the electrolyte to interact with and produce SEI materials, affecting power density.⁴ Anode material taken from commercial electrodes was thermally treated to remove all CMC/SBR, and images to show whether damage had occurred during recovery. Figure 4-4 shows two electrodes, one made from pristine graphite, and one made from reclaimed graphite. The reclaimed graphite shows evidence of increased amounts of particle fracturing, indicating that the high-powered ultrasonic recovery process has altered the material. While fracturing is likely to increase the surface area of the individual graphite particles, particle size measurements show that the average particle size is actually increased for the reclaimed graphite (Table 4-3). This implies that localised agglomeration is occurring, lowering the surface area of the material and hence the number of available lithium intercalation sites, ultimately decreasing the cell capacity during all electrochemical testing. However, it is also observed that there is a greater variability in the particle size measurements when a great proportion of the active material is reclaimed graphite. This implies a large proportion of inhomogeneity within the electrode, with some areas showing larger surface areas due to fractured particles and others showing a diminished surface area when those particles agglomerate together. This inhomogeneity in the graphite particles could potentially result in some degree of electrochemistry localisation, which could lead to undesirable effects such as inconsistent SEI formation and intercalation/deintercalation occurring at different rates during charge/discharge.²⁶



Figure 4-4: SEM images of the remanufactured anodes created using a) 100% pristine graphite and b) 100% reclaimed graphite.

Table 4-3: Particle size analysis taken for anode materials using different ratios of pristine
reclaimed graphite and NaAlg as the binder.

P:R Graphite	Average Particle Size (μm)	Standard Deviation
100 : 0	14.8	3.5
80:20	15.0	3.8
50 : 50	15.0	3.6
0:100	15.8	6.4

Half cells were made using different blends of pristine and reclaimed graphite, with sodium alginate as the binder material. These were cycled using the same conditions as for the pristine graphite, and example voltage profiles are shown in **Figure 4-5** for each of the graphite blends. During the formation cycles, voltage profiles are obtained similar to those in **Figure 4-2**, with voltage plateaus corresponding to the different stages of lithium intercalation observed between 0.0 V and 0.25 V. The feature assigned to electrolyte decomposition is also observed at ca. 0.7 V during cycle 1 for all electrode compositions and is absent from the voltage profile of cycle 5. This, paired with the increase in Coulombic efficiency shown in **Table 4-4**, indicates that the SEI layer successfully forms and is effective at limiting further electrolyte decomposition during future cycling, even when 100% reclaimed graphite is used.



Figure 4-5: Voltage profiles for the remanufactured anode half-cells using different pristine:recycled graphite ratios and NaAlg as the binder, a) 80:20, b) 50:50, c) 0:100. The 100:0 profile is given in Figure A1c.

Despite the evidence of SEI formation and lithium intercalation for all electrode compositions, the charge/discharge capacities obtained from the half cells containing reclaimed graphite all indicate a reduction in cell performance. For example, there is a drop of ca. 30-40 mAh.g⁻¹ in average charge/discharge capacity of cycle 5 when 100% reclaimed graphite is used. This correlates to a cell capacity of only 87% of one formed from 100% pristine graphite. While the exact mechanism of the decrease in capacity is unclear, it is highly likely that the inhomogeneities brought about from particle fracturing and agglomeration are influencing this behaviour. For instance, areas of low surface area will decrease the diffusion of lithium into the electrode structure due to a limited amount of available intercalation sites. Additionally, as these agglomerations are made of smaller particles encapsulated by the binder, these may become electronically isolated and inactive, which would further diminish cell capacity. A similar mechanism has been observed when electrolytes containing propylene carbonate are used. In these instances the electrolyte species can be reduced in the presence of lithium ions,

forming an additional passivating layer on the graphite particles, electronically isolating them.²⁷

Table 4-4: Formation cycling data for half-cells with each of the all pristine:recycled graphite ratios investigated in this study. Charge and discharge capacities were obtained by taking an average of multiple coin cells, the standard deviation given in brackets. 'Charge' refers to the movement of lithium into the graphite.

Pristine: reclaimed Graphite Ratio	Cycle Number	Average Charge Capacity (mAh.g ⁻¹)	Average Discharge Capacity (mAh.g ⁻¹)	Average Coulombic Efficiency (%)
100:0	1	319 (21)	280 (21)	87.6 (0.8)
	5	305 (2)	293 (2)	96.0 (0.1)
80:20	1	283 (24)	255 (21)	87.9 (1.6)
	5	299 (11)	291 (9)	97.2 (1.3)
50:50	1	259 (9)	219 (10)	84.6 (1.9)
	5	282 (18)	272 (20)	96.3 (1.3)
0:100	1	234 (11)	210 (19)	86.2 (2.7)
	5	266 (15)	259 (11)	97.5 (1.5)

Further testing was carried out to determine how different C-rates and cell ageing affected the capacities of these cells and whether the longevity of the cells is severely diminished due to the potential capacity fade mechanisms previously discussed. **Figure 4-6** shows the waterfall plots for each anode composition investigated. The cell capacities recorded at a cycling rate of 0.1 C decrease as a function of the amount of reclaimed graphite used in the anode, and the waterfall plots confirm that performance at higher cycling rates is also diminished. While it is assumed that the aforementioned capacity fade mechanisms are the cause of the poor rate capability of the anodes using the reclaimed graphite, it should be noted that poor lithium diffusion resulting from higher electrode surface areas is more prevalent at these higher C-rates. These agglomerations of graphite, conducting additive, and undissolved binder material from the source material also exacerbate the limitations of graphite at high cycling rates, causing the rapid capacity reduction in the rate testing, reducing the cycling rate the cells are stable at from 0.5 C to 0.2 C as the amount of recycled graphite is increased. Also, the anodes using reclaimed graphite show rapid capacity fade over 20 cycles when compared

to pristine materials, showing a 20-30% drop in capacity versus an 8% reduction for the pristine material (**Table 4-5**). Observing how impedance contributions change with cycling across the interfacial regions for the cells using reclaimed material will allow a conclusion to be made on the major effects that are limiting capacity of these cells during the rate tests and long-term cycling. It will also allow determination of whether there is a substantial change in the impedance arising from changes to the SEI layer that may also be caused from inhomogeneous particle sizes and surface areas compared to the pristine sample, which may also be limiting lithium intercalation.



Figure 4-6: Waterfall plots showing how the C-rate applied to the half-cells affects the capacity (mAh.g⁻¹). Black symbols show graphite charging, red outlines show graphite discharging. a) 100:0, b) 80:20, c) 50:50, and d) 0:100.

P:R Ratio	Capacity Retention (%) at Cycle 5	Capacity Retention (%) at Cycle 10	Capacity Retention (%) at Cycle 20
CMC/SBR Reference	97.3 (0.4)	90.9 (1.7)	88.9 (4.7)
100:0	98.6 (0.4)	96.9 (0.7)	92.2 (3.1)
80:20	95.0 (3.3)	83.7 (5.6)	70.3 (4.8)
50:50	95.9 (0.2)	84.0 (2.0)	78.3 (3.7)
0:100	93.6 (0.7)	86.2 (0.4)	73.1 (5.4)

Table 4-5: Capacity retention data (%) for anodes using different pristine:recycled (P:R) graphite ratios and a NaAlg binder over the course of 20 cycles at a C-rate of 0.1 C. The CMC/SBR data from Table 4-2 is used as a reference.

4.4 <u>Electrochemical impedance studies</u>

EIS measurements were taken for each sample in this study after both the formation cycles and the rate testing, which allows analysis of the cells after the formation of components such as the SEI layer in the initial cycles. Previous studies into the effect the binders have on impedance measurements were used to form the basis of this analysis,²⁸ which included identification of the key impedance contributors that will be discussed by data modelled from the Randles circuits given in **Figure 4-7**. These impedances contributions are; R_S – resistance of the cell components, electrode and electrolyte, R_{SEI} – resistance of the SEI layer and R_{CT} – charge transfer resistance across the electrode-electrolyte interface. In these samples an additional contributor is also observed for the gelatin-based anodes, this has been defined as R_L - resistance of the polymeric/carbon black coating found on the electrode surface.



Figure 4-7: Randle circuits used for EIS modelling. a) used for anodes containing PVDF, CMC/SBR, NaAlg and DES-modified NaAlg binders, b) used for anodes using gelatin and DES-modified gelatin binders.

The Nyquist plots obtained for all the samples in this study (**Figure 4-8** and **Figure 4-9**) show the same general appearance to that seen for other LIB impedance investigations, with flattened semi-circle structures and an uptick in the low frequency region, indicative of porous graphitic anodes. Generally, the R_s values (**Table 4-6**) for each sample are of a similar magnitude, which would be reasonable as the same cell components and electrolyte are used regardless of the samples. There are a few exceptions, for example the CMC/SBR and gelatin 100 cells show higher values. While it is unclear what causes this increase, it could be related to poor electrical contact within the cells, an issue that has been observed in literature for CMC/SBR in other electrode chemistries previously.²⁹ There is also a reduction in the R_s values of NaAlg and DES-modified binder systems compared to PVDF. Previous work into DES-modified systems, and this increased level of adhesion could be improving electrical contact of the cell.³



Figure 4-8: Nyquist Plots taken after each electrochemical test to show how impedance changes with regards to each interfacial region. Data was obtained at 0.1 V, between 300,000 Hz and 0.1 Hz. Not all plots are shown for the DES-modified binders, representative curves are shown. a) PVDF, b) CMC/SBR, c) gelatin 90, and d) NaAlg 90.

It is thought that the effects each binder has on R_{SEI} and R_{CT} rather than R_S will be more important in explaining the electrochemical behaviour detailed in the previous sections. In the case of R_{SEI} , all samples, except the anodes using DES-modified NaAlg, show increased resistances of between 2-3 Ohm after rate testing. These increases can relate to a number of different processes, including: a) the SEI layer is still developing during the rate test, including electrolyte and/or binder decomposition, b) the graphite particles are undergoing a physical change, such as loss of contact, cracking, or c) changes are happening to the electrode surface, such as variation in porosity or a decrease in electrode surface area.^{30,31} While the R_{SEI} increased for the NaAlg 100 sample, the final value after rate testing is similar in magnitude to the DES-modified samples (NaAlg 90 and NaAlg 80). A smaller impedance value for this contribution has also been observed in other studies, where electrodes containing NaAlg possessed thinner SEI layers and exhibited better electrical contact than conventional materials.³² It is unclear why the DES-modified NaAlg cells show a higher R_{SEI} impedance value after formation cycling, or why this value decreases after the rate tests, unlike the other cells analysed. It is possible that the DES-modified NaAlg samples form a less stable SEI layer, however the higher capacity retention compared to gelatin cells, which show more stable R_{SEI} values, disputes this. Also, unlike the other cells, the R_{CT} values for the NaAlg samples mostly remain stable before and after rate testing and are lower than the other anodes tested. Both of these observations could be related to the dielectric properties and interchain free volume improvements additives can have on anodic binders, which is theorised to be the reasoning behind the improved rate capability of the DES-modified NaAlg binders.²³ Previous impedance studies have shown that electrodes using binders with additives such as glycerol, which is present in the DES, reduce the R_{CT} values correspond to the NaAlg 90 sample, which could imply that the ion transport is most optimal at this DES content might help to explain the different impedance values obtained for the electrodes, DES content does not seem to have a significant impact on the rate capability of the cells.

However, the most notable observation made with the impedance data shown for the pristine graphite study is the additional impedance contribution relating to an additional charge transfer process, RL, in electrodes containing gelatin as the binder. It is assumed this contribution relates to the movement of lithium ions through the polymeric coating only seen in the gelatin materials. The impedance relating to this layer increases with additional cycling, which could be related to porosity changes with cell ageing or the breakdown of the polymer after high cycling rates.³⁰ Interestingly, when DES is present there is less of an increase to this impedance contribution before and after rate testing. As was hypothesised for the NaAlg samples, the presence of the DES may facilitate ion transport through this additional particle coating, and also improve R_{CT}, where a decrease in impedance can be observed after the rate test. Ultimately, the EIS results show that the presence of DES in both the NaAlg and gelatin samples improves the impedance characteristics of the anodes by lowering R_{SEI} and R_{CT}. It is also notable that the coating behaviour of gelatin towards the graphite particles is significant enough to contribute resistances comparable in size to that of the SEI layer, with the increased resistance to ion diffusion presumably causing the much poorer rate capability of the gelatin anodes. Therefore, the differences in electrochemistry and rate capabilities between the different binder formulations are not necessarily related to the SEI composition or formation alone.

Table 4-6: Modelled EIS resistance data for the Nyquist plots shown in Figure 4-8, using the Randles circuits given in Figure 4-7. EIS measured after the initial formation cycles and after rate testing. The values presented are using the circuit that models the EIS response best. Errors in fits are given in brackets.

Binder System	Rs (Ω)	Rsei	(Ω)	RL (Ω)	$\mathbf{R}_{\mathrm{CT}}(\mathbf{\Omega})$		
	Formation	Rate Test	Formation	Rate Test	Formation	Rate Test	Formation	Rate Test	
PVDF	3.92 (0.03)	4.73 (0.12)	5.68 (0.06)	8.46 (0.16)	_	_	8.25 (0.08)	7.42 (0.07)	
CMC/SBR	4.18 (0.04)	10.5 (0.1)	6.86 (0.28)	8.06 (0.19)	-	-	17.2 (0.3)	9.39 (0.16)	
Gelatin 100	5.31 (0.03)	6.43 (0.18)	2.26 (0.21)	6.49 (0.24)	6.82 (0.54)	8.17 (0.80)	2.27 (0.22)	7.29 (0.67)	
Gelatin 90	3.57 (0.01)	2.69 (0.27)	3.23 (0.42)	5.53 (0.11)	4.76 (0.89)	4.94 (0.48)	9.35 (0.32)	6.16 (0.60)	
Gelatin 80	2.36 (0.01)	5.20 (0.10)	2.49 (0.12)	4.93 (0.45)	4.96 (0.20)	5.53 (0.55)	9.62 (0.10)	5.44 (0.53)	
NaAlg 100	1.85 (0.01)	3.26 (0.03)	1.40 (0.06)	4.08 (0.08)	-	-	5.12 (0.05)	5.07 (0.06)	
NaAlg 90	3.69 (0.02)	5.39 (0.02)	7.87 (0.22)	4.30 (0.08)	_	_	3.12 (0.22)	3.72 (0.07)	
NaAlg 80	2.48 (0.05)	3.41 (0.10)	6.28 (0.61)	4.18 (0.18)	-	_	20.4 (1.0)	5.19 (0.11)	

Impedance measurements were also carried out on the cells containing reclaimed graphite active material at the different compositions described previously, in order to determine the root causes of the reduced capacity and diminished rate capability seen in **Figure 4-6**. In all cases the Nyquist plots showed similar behaviour to that of the anodes formed from pristine graphite, with two flat semicircles and an uptick in the low frequency region. **Figure 4-9** shows the specific plots obtained in these experiments and **Table 4-7** shows the resulting impedance data obtained from modelling. In general, the impedance data for the reclaimed graphite shows similar trends to the unmodified cell data in **Table 4-6**. The majority of the trends in the impedance before and after the rate test are similar, regardless of the composition of pristine:recycled graphite. The main difference is the increased magnitude of the impedance values before the rate test, although after the rate tests these values starting higher for the reclaimed graphite anodes is thought to be related to the electrical isolation of the agglomerations and the inhomogeneous surface area causing irregular electrolyte decomposition.



Figure 4-9: Nyquist Plots taken after each electrochemical test to show how impedance changes with regards to each interfacial region. Data was obtained at 0.1 V, between 300,000 Hz and 0.1 Hz. a) 100:0, b) 80:20, c) 50:50, d) 0:100

While extensive cycling of these cells results in impedance values comparable to pristine graphite, the inhomogeneities of the reclaimed material will likely have an impact on R_{CT}, the value of which increases with the proportion of reclaimed graphite in the electrode. The movement of the lithium ions across the electrode-electrolyte interface is also likely to be affected by the inhomogeneity of the electrode surface and the isolation of a significant proportion of the active material. In other systems using composite anode systems, with various surface areas, inhomogeneities that arise present the localisation of electrochemistry, which facilitates localised structural defects, voltage gradients across the electrodes, electrode cracking and could even result in lithium plating.³⁵ All effects are capable of limiting lithiumion transfer into electrode systems and are often self-propagating processes. The localisation is thought to be occurring at areas of higher surface area, but it should be noted that this effect may be propagated further by electrical isolation of the agglomerated particles, blocking lithium intercalation sites by the binder and forbidding lithium intercalation. While it is notable that all the impedance values shown in Table 4-7, regardless of the amount of reclaimed graphite used, are slightly smaller in magnitude to that of PVDF and CMC/SBR anodes in Table 4-6, it is predicted that the impedance rise mechanisms discussed will become increasingly dominant with further cycling and may surpass the impedance rises observed for these commercial binders.

P•B	R _S (G	2)	Rsei (S	2)	$R_{CT}(\Omega)$		
Ratio	Formation	Rate Test	Formation	Rate Test	Formation	Rate Test	
100:0	1.85	3.26	1.40	4.08	5.12	5.07	
	(0.01)	(0.03)	(0.06)	(0.08)	(0.05)	(0.06)	
80:20	3.07	5.10	3.97	4.87	5.56	4.20	
	(0.07)	(0.14)	(0.08)	(0.23)	(0.19)	(0.10)	
50:50	3.19	2.68	3.96	3.92	6.32	5.46	
	(0.02)	(0.08)	(0.21)	(<i>0.17</i>)	(0.18)	(0.12)	
0:100	3.25	5.96	2.96	4.78	8.13	6.36	
	(0.02)	(0.18)	(0.09)	(0.37)	(0.08)	(<i>0.19</i>)	

Table 4-7: Table showing the modelled data for the Nyquist plots shown in Figure 4-9using the Randle circuits given in Figure 4-7.

4.5 <u>Conclusions</u>

This study has shown that the use of DES-modified NaAlg and gelatin binders does have an effect on the electrochemical performance of graphite anodes in lithium half cells compared to those made with commercial PVDF and CMC/SBR binders. During formation cycling, all cells tested showed comparable capacities and Coulombic efficiencies to each other, indicating that, regardless of the binder or amount of DES used, lithium ions were able to reversibly intercalate into the graphite, and SEI formation and growth was occurring at a similar rate. When assessing the rate capability of the cells, anodes containing the NaAlg and gelatin binders showed opposite behaviours. Unmodified NaAlg (NaAlg 100) cells showed comparable performance to PVDF and CMC/SBR cells, where capacity approximately halves when the cycling rate is increased from 0.5 C to 1 C. However, upon modification with the DES, the rate capability of the NaAlg 90 and NaAlg 80 cells increased, showing a capacity ~ 70 mAh.g⁻¹ higher at 1 C compared to anodes made using PVDF and NaAlg 100. On the other hand, the gelatin-based anodes showed diminished performance, only showing stability at low cycling rates, up to 0.2 C, which was not improved with the addition of DES. This deviation in performance was presumed to be related to the differences in the location of the polymers within the anode, with

gelatin forming a polymeric coating on the particles, which is seen in the EIS data through an extra impedance contributor, denoted as R_L. Long term cycling carried out over 20 cycles further solidified the superior performance of the cells using NaAlg-based binders compared to those using gelatin. Capacity losses were substantial for anodes using gelatin, between 20-40%, which were minimised to between 5-8% for cells containing NaAlg systems. These results showed the viability of NaAlg-based binder systems.

Anodes were also prepared from reclaimed graphite from commercial sources using a novel ultrasonic delamination technique. These cells showed diminished rate performance, similar to the gelatin-based materials and showed increased impedance compared to cells made with pristine graphite. This behaviour is thought to be related to the fracturing and agglomeration of graphite particles caused by ultrasound. Possible effects on the electrochemistry were discussed, including the electrical isolation of particles due to polymer encapsulation and irregular SEI growth causing localised electrochemistry, which is capable of causing numerous other detrimental phenomena, such as structural defects and lithium plating. Therefore, a gentler technique is required to reclaim the graphite, which will be aided by the use of watersoluble binders such as sodium alginate.

4.6 <u>References</u>

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Chapter 5: Characterisation of polyaniline-water soluble polymer blend binders in lithium-ion battery anodes

5.1 Introduction

The previous chapters discussed the modification of polymers using a deep eutectic solvent to optimise adhesive strength and thermal stability of the resulting electrode. Another key property that is investigated in relation to the binders within electrodes is their conductivity, with the amount of binder often being minimised to optimise the conductivity of the electrode as much as possible. Previous studies have attempted to incorporate conducting binders into electrode systems, with one such example being a poly(3,4-ethylenedioxythiophene) (PEDOT) - poly(styrene sulfonate) composite.^{1,2} While these materials showed good electrochemical stability and can be processed in aqueous conditions rather than using toxic solvents, such as NMP, the cost of these materials are roughly 300 times more expensive then commercial lithium-ion battery (LIB) binders like PVDF. Therefore the use of other, more cost effective, conducting polymers such as polyaniline (PANI) have been investigated as binders and active materials.^{3–5} Additionally, PANI composites materials with graphite (as well as molybdenum oxide) have shown increased conductivity compared to pure PANI, due to the material allowing excess charge to be dispersed between the two components.⁶ The same concept could be utilised in battery electrode materials to improve performance and stability of anodic materials.

The structure of PANI is shown in **Figure 5-1a** and **Figure 5-1b**, which presents the process of how the polymer is doped in order to formulate the conducting form of the material, going from the emeraldine base (EB) to the emeraldine salt (ES). Essentially, the ES conducts electrons through the formation of polarons and bipolarons, charge carriers, which conduct electrons via inter/intra chain migration of the charge on the polymer backbone.⁴ Blending PANI with a water-soluble polymer could allow for these polarons to improve conductivity of the binder regions within an electrode, whilst also retaining the processibility benefits of utilising water-soluble binders and the other physical and mechanical benefits shown in the previous chapters. A previous study by Bhadra *et al.* showed the formation of polymer films using PANI and various water-soluble polymers, including sodium alginate (NaAlg).⁷ This investigation showed an improvement to the conductivity of NaAlg without need for a complicated formulation

procedure, only requiring heating and stirring, with brief sonication. This simple procedure could be easily adopted into the formulation of LIB electrodes without complicated or expensive reaction conditions, or the large onset costs associated with establishing new methodologies and technologies.



Figure 5-1: Molecular structure of PANI in a) the reduced state, b) the oxidised state and c) PEG. This also shows the formation of polarons on the PANI polymer backbone responsible for electron transfer and conducting properties by going from a) and b).

The aim of this chapter is to characterise the polymer blends formed from PANI and different water-soluble polymers, beginning with NaAlg and gelatin before exploring polyethylene glycol (PEG) which has also had some interest as a possible binder in LIBs (molecular structure for PEG shown in **Figure 5-1c**).^{8,9} The same methodology used in the paper by Bhadra *et al.* is utilised to form polymer blend films at different PANI compositions. This was done to create a simple and cost effective PANI-binder system, instead of the complex 3D matrices and polymerisation onto carbon nanotubes investigated previously.^{10,11} These films were analysed to determine their conductivity (4-point probe), mechanical stability (scratch test), chemical structure (FTIR) and thermal stability via both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Topography and modulus imaging was then carried out with atomic force microscopy (AFM) to observe polymeric changes in the films as a result of the addition

of PANI. Once the films are analysed the polymer blends will be incorporated into LIB graphite electrodes in a similar manner to the previous chapters. The morphology and the location of the binder will be determined via scanning electron microscopy (SEM) and AFM. The scratch test will then be used to determine the adhesive strength of the electrodes as a function of PANI content. Electrochemical characterisation of these electrodes is then carried out via electrochemical impedance spectroscopy (EIS) and coin cell cycling to observe the solid electrolyte interface (SEI) layer formation, new cell capacity and capacity retention. Lastly, recyclability will be tested via ultrasonication techniques established by Lei *et al.*, used in chapter $3.^{12}$

5.2 Characterisation of PANI blend films

Initially, the PANI polymer blends were made into polymer films and cast onto microscopy slides to be analysed in isolation before their incorporation into electrode materials. This is to observe any important changes to their inherent chemical structure, conductivity, and mechanical and thermal stabilities. Adding different amounts of PANI to the films was done first to determine the optimal concentration to maximise conductivity whilst retaining film stability.

5.2.1 Conductivity

PANI polymer blends were created using the methodology outlined in the paper by Bhadra *et al.*.⁷ In order to determine the ideal PANI concentration within the blends to maximise conductivity a range of different PANI:polymer ratios were used for each of the tested polymers; NaAlg, gelatin and PEG. The different amounts of PANI tested in the polymer films were 10 wt%, 20 wt%, 30 wt% and 40 wt%, however only the 10 wt% and 20 wt% compositions formed cohesive films and will be the only systems discussed in this work. Additionally, whilst NaAlg, gelatin and PEG were tested as the base polymer for the films, only the NaAlg and PEG films resulted in conducting materials, measurable via the 4-point probe. So, gelatin was no longer investigated past this point.

Table 5-1 summarises the conductivity data for the PANI:NaAlg and PANI:PEG polymer blends, along with a respective reference polymer film created using the same methodology, minus the addition of any PANI. In the case of the NaAlg-based films, the conductivity is increased when 10 wt% PANI is added. The resulting conductivity value closely resembles that found in the study this methodology is based on, where a similar composition of NaAlg-to-PANI was used.⁷ Upon doubling the PANI content to 20 wt%

the conductivity value obtained also doubles compared to the 10 wt% sample. It is anticipated that the increased availability of the polarons and bipolarons as more PANI is added to the system is responsible for these stepwise increases to conductivity. Similarly, the PEG-based films also show improvements to the conductivity with increasing PANI concentration, albeit at a smaller magnitude, where the PANI:NaAlg (20 wt% PANI) sample is 50 times greater than PANI:PEG (20 wt% PANI). However, the conductivity of the PANI:PEG is still notable due to the non-conducting nature of the reference PEG film, implying that the insertion of PANI into the polymer matrix is solely responsible for film conductivity, unlike NaAlg.

Table 5-1: Conductivity data from a 4-point probe showing conductivity changes as a function of the base polymer used and the PANI content incorporated. Values in brackets and italics represent error values, determined by taking a standard deviation of all the conductivity measurements.

PANI Blend	Conductivity (S cm ⁻¹)
NaAlg Reference	8.10 x 10 ⁻⁷ (3.75 x 10 ⁻⁸)
PANI:NaAlg (10 wt% PANI)	2.42 x 10 ⁻⁶ (3.92 x 10 ⁻⁸)
PANI:NaAlg (20 wt% PANI)	4.81 x 10 ⁻⁶ (1.09 x 10 ⁻⁷)
PEG Reference	0
PANI:PEG (10 wt% PANI)	8.00 x 10 ⁻⁸ (1.24 x 10 ⁻⁹)
PANI:PEG (20 wt% PANI)	1.20 x 10 ⁻⁷ (1.08 x 10 ⁻⁶)

The current versus voltage curves obtained from the 4-point probe for the NaAlg and PEG reference films and PANI blend films are seen in **Figure 5-2**. Each film was analysed with regards to a target current of 5.00×10^{-8} A, hereby the more conducting the sample, the lower the voltage required to reach this target. **Table 5-1** shows that NaAlg is inherently conducting, prior to PANI addition, while **Figure 5-2** shows the nature of that conductivity to be similar to that of a semi-conductor, where either side of a 'zero point' there is a significant rise (forward characteristics) or fall (reverse characteristics) in current with a relatively small voltage change. The inherent semi-conducting behaviour of NaAlg has previously been attributed to the presence of ionic functional groups, which

form ionic inter-chain 'bridges' throughout alginate hydrogels. It is likely a similar effect is occurring in these films.¹³ Similar curves are observed in semi-conductor diodes as well as with conjugated conducting polymers, such as PANI.^{14,15} It is thought that the similar appearances of the current/voltage curves for NaAlg and PANI is the reason why minimal changes are seen in the curves before and after PANI incorporation. The forward internal barrier voltage, the voltage that needs to be exceeded before the sharp rise in current, is 3.05 V for the pure NaAlg and 2.57 V when 20 wt% PANI is present. This value along with the lower resistance experienced after this voltage is met, seen by the gradient of the curve, results in the higher conductivity of the PANI:NaAlg sample. In the case of the PANI:PEG film, while the curve still resemblances that of a semi-conductor, the lack of a distinct plateau and the defined barrier voltages contrasts that seen in the NaAlg samples. Additionally, the gradient changes experienced by this curve is also thought to be a result of the non-conducting nature of the base polymer interfering with the current flow of PANI. Note that data was collected for a PEG reference film but no reading could be completed as the binder is inherently non-conducting.



Figure 5-2: Current vs. voltage curves, showing the electrical conductivity behaviour of a sodium alginate (NaAlg) reference film, PANI:NaAlg with 20 wt% PANI film and a PANI:Polyethylene glycol with 20 wt% PANI film. All samples were set a target current of 5 x 10^{-8} A to acquire the curves.

The conductivity data summarised here indicates that the blending of PANI with the base polymers, NaAlg and PEG, has been successful, at least to the extent of enhancing the conductivity of the polymer films. This enhancement to conductivity is thought to be primarily due to the PANI distribution aiding, or causing in the case of PEG, current to flow within the films. In both cases the presence of PANI is significant, making PEG films electroactive and significantly enhancing the conductivity of NaAlg. It is thought that the higher concentration of the polarons within the films as a result of PANI concentration is the source of these benefits to conductivity.

5.2.2 Mechanical Characterisation

A key factor in the investigation into PANI polymer blends, rather than using pure PANI, as a binder within electrode materials is the mechanical stability of the polymer, which is closely related to its chemical structure, seen in **Figure 5-1**. The PANI polymer backbone possesses a large number of aromatic rings and double bonds making it relatively stiff and brittle.¹⁶ These intrinsic characteristics are the reason for many studies focusing on polymer blends and co-polymers involving PANI in technological applications rather than the pure polymer, in order to combine the electrical properties of PANI with the processability and mechanical characteristics of other polymers.^{17,18} In order to quantify the effect that PANI has on the mechanical integrity of the polymer blend films, the scratch test was used to determine the cohesive strength of the polymers. **Table 5-2** shows the data for the NaAlg and PEG reference materials as well as reference data for commercial LIB binders, PVDF and CMC/SBR for reference. In this case the critical load is defined as the load where the film has been ruptured and the microscopy slide glass is visible on a 3DM.

	also given.	
PANI Blend	Critical Load (N)	% Difference in Critical Load
NaAlg Ref	7.87 (0.13)	-
PANI:NaAlg (10 wt% PANI)	6.88 (0.81)	- 12.6 %
PANI:NaAlg (20 wt% PANI)	4.97 (0.48)	- 36.8 %
PEG Ref	3.20 (0.36)	-
PANI:PEG (10 wt% PANI)	3.57 (0.04)	+ 11.6 %
PANI:PEG (20 wt% PANI)	2.76 (0.22)	- 15.9 %

Table 5-2: Scratch test data showing the critical load of the PANI polymer blend polymer films at 10% and 20% PANI content for both the sodium alginate (NaAlg) and polyethylene glycol (PEG) samples. % difference compared to reference films is also given.

Table 5-2 shows a clear reduction in cohesive strength for both the NaAlg and PEG based films as more PANI is added, however it was expected that the mechanical stability would be somewhat compromised to improve the conductivity with PANI. For the NaAlg blends this is quite significant, with the critical load dropping by around 3 N with a 20 wt% addition of PANI. Meanwhile, for the PEG samples there is an initial increase in cohesive strength upon 10 wt% PANI being added, before a drop when it is increased to 20 wt%. The general decrease is likely a result of some degree of disruption to the interchain interactions and cross-linking for both polymer systems. Meanwhile, the improvement to the cohesive strength when 10 wt% PANI is added to PEG could be related to significant changes to chemical structures or morphology as a result of the incorporation of PANI. These changes could result in the formation of new interactions that lead to a slightly improved critical load upon small additions of PANI. Then, when PANI content is increased further even these interactions are broken apart. The overall reduction in the cohesive strength of the films was expected when PANI was added. However, the degree in which this has occurred is significant and is expected to affect the mechanical integrity of the anode materials created using these polymer systems as the binder.

5.2.3 Infrared spectroscopy characterisation

In order to determine what effect, the presence of PANI has on the chemical structure of the base polymers within the films, FTIR was carried out. The key transitions will be discussed in relation to the reference films before any changes to the wavenumbers of these transitions, brought about by the PANI, are detailed. **Figure 5-3** shows the FTIR spectra for the NaAlg-based films, **Figure 5-4** shows the PEG-based films and **Table 5-3** details the wavenumber transitions for the key functional groups present within the base polymers and PANI.

The most notable observation from the PANI reference FTIR spectra was the absence of peaks present in the literature.¹⁹ Transitions between 3400-3200 cm⁻¹, 3100-2800 cm⁻¹ and 2800-2300 cm⁻¹ corresponding to N-H stretching, C-H stretching and the presence of iminium (C=N⁺) groups were missing respectively. This form of PANI is the ES, shown in **Figure 5-1b**, so the C=N+ is replaced by a protonated C-N+ stretching transition, seen at a lower wavenumber of 1286 cm⁻¹.²⁰ However, the other two missing transitions, N-H and C-H, are still expected to be seen. The relatively low transmittance

observed in the PANI spectra could be masking these missing peaks, as they are known to be relatively shallow and broad transitions, whilst retaining the larger, more pronounced peaks of functional groups active at the lower wavenumbers. Therefore, it is assumed these groups are present, even though they cannot be observed. Furthermore, the peaks observable at 1556 cm⁻¹ and 1416 cm⁻¹ have been attributed to the characteristic stretching of the quinoid and benzenoid structures upon the PANI backbone.^{19,21} Lastly, the low frequency transitions, including the peak at 1068 cm⁻¹, are due to the delocalisation of electrons and the bending of aromatic carbons throughout the backbone.²²

The FTIR analysis of the NaAlg reference film is similar to that of the unmodified NaAlg binder detailed in chapter 3, with the same previous study being used as a starting point.²³ The peak at 3179 cm⁻¹ is related to an O-H stretch and the smaller transition at 2915 cm⁻¹ has been identified as a C-H stretch of the cyclic carbons present on the polymer backbone. The transition at 1403 cm⁻¹ is attributed to the bending of these C-H groups, with the noise present within this region being associated with the multiple, C-H groups present on the alginate backbone. The transition at 1593 cm⁻¹ corresponds to an asymmetric stretch of the –COO⁻ group, while the last two significant transitions at 1079 cm⁻¹ and 1023 cm⁻¹ are related to the C-O and C-OH/C-C-O stretches respectively.



Figure 5-3: IR Spectra obtained from the NaAlg-based PANI polymer films. The samples analysed include the 10 wt% and 20 wt% PANI:NaAlg films along with PANI and NaAlg reference spectra.

The FTIR spectra indicates that the addition of PANI into the NaAlg films has a minimal impact on the NaAlg structure. Wavenumbers stay constant for the majority of the functional groups as seen in Table 5-3, and the main deviation in Figure 5-3 between samples is the peak intensity rather than peak shifting. Peak shifting is only observed for the broad O-H/N-H transition and the associated CH stretch. It is predicted these shifts are due to the presence of the PANI, rather than any reaction between the PANI and NaAlg. This is because both N-H and O-H groups absorb infrared radiation at similar frequencies, resulting in them overlapping in the IR spectra. Due to the fact that N-H groups from the PANI cause a peak at slightly higher frequencies, the increasing concentration of PANI and the N-H groups results in the shifting of the peak to higher wavenumbers. This broad peak (> 3000 cm^{-1}) even seems to start separating into two peaks relating to N-H (> 3300 cm⁻¹) and O-H groups (3000-3300 cm⁻¹) in the 20 wt% PANI sample as a result of this increased presence of N-H. However, previous studies have shown that a shift in the transition corresponding to the -OH groups within NaAlg can also be a result of weakening of polymer-polymer interactions.²³ This means these shifts could be related to the weakening of the -OH hydrogen bonding, similar to how the -COO⁻ transition behaved when NaAlg was modified with a DES in chapter 3.



Figure 5-4: IR Spectra obtained from the PEG-based PANI polymer films. The samples analysed include the 10 wt% and 20 wt% PANI:PEG films along with PANI and PEG reference spectra.

For the PEG reference spectra, the peak at 2877 cm⁻¹ relates to C-H stretching, the transitions between 1500 cm⁻¹ and 1300 cm⁻¹ correspond to C-H bending and the main low frequency peak at 1096 cm⁻¹ is attributed to the stretching of the C-O bonding.²⁴ Similar to NaAlg, the presence of PANI causes minimal impact on the location of the IR transitions. The main difference before and after PANI addition is the presence of the peaks relating to PANI, including peaks missing from the PANI reference spectra, implying that the loss of these peaks in that spectra was a transmittance issue. One observed peak at 2700 cm⁻¹ is notable as it corresponds to the iminium group ($C=N^+$). For the ES of PANI this group is formed/de-formed via rearrangement reactions when polarons 'migrate' throughout the polymer chains. This group is presumed to be present in the NaAlg systems but is not seen in the spectra due to it being masked by the O-H transition. Interactions between PANI and the two polymers could also be explained by the presence of this iminium group. Polarons, characteristic of the ES form of PANI, possess lone electrons that could interact with various groups on the base polymers, -OH and -COO⁻ groups on NaAlg and -OH and ether groups on PEG. The weakened cohesive forces of the polymer films when PANI is present could also be related to these interactions disrupting other polymer-polymer interactions that occur via these groups within the base polymer structure.²³

		Functional Group Stretches (cm ⁻¹)											
Base Polymer	wt% of PANI	O-H/ N-H Stretches	-CH Stretch	C=N+	C=O Stretch	Asymmetric COO ⁻	N=Q=N Stretch	C-H Bending	Bending of CH2	CN Stretch	C-O Stretch	Aromatic C-N-C Bending	C-OH/ C-C-O Stretches
PANI	Reference	_*	-	_*	1682	-	1556	1416	-	1286	-	1068	-
NaAlg	Reference	3179	2915	-	-	1593	-	-	1403	-	1079	-	1023
	10	3244	2932	2742	-	1592	-	-	1406	1296	1081	-	1025
	20	3262	2926	2743	-	1592	-	-	1406	1295	1080	-	1024
PEG	Reference	-	2877	-	-	-	-	1466 1359	-	-	1096	-	N/A
	10	3408 3228	2880	2738	1715	-	1556	1465 1359	-	1278	1100	1058	-
	20	3410 3233	2875	2739	1731	-	1556	1465 1359	-	1278	1094	1058	-

Table 5-3: Table showing the wavenumbers attributed to the key functional group stretches for the NaAlg and PEG based PANI polymer blend films along with the respective pure polymers for reference.

*Signifies a transition which is present in literature but no reading was observed in this study.

5.2.4 Atomic force microscopy images

In order to determine whether the reduced cohesion of the PANI polymer blends could be influenced by changes to the topography and macro-structure, AFM was carried out, using the methodology detailed in chapter 3.^{25,26} AFM was used to image the film surfaces to avoid damage to the samples that could be incurred when electron-based microscopy methods are used. Modulus scans, as well as topography imaging was attempted but due to the similarity in the Young's modulus of the PANI and base polymers no distinction could be made. **Figure 5-5** shows the topographical images for the base polymer reference films and the PANI blend films utilising 10 wt% PANI. The films using 20 wt% PANI were also investigated but no observable topographical difference was observed between 10 wt% and 20 wt% PANI.



Figure 5-5: AFM imaging of the polymer films investigated in this section, both with and without PANI content to observe topographical changes to the material. a) NaAlg reference, b) PANI:NaAlg (10 wt% PANI), c) PEG reference and d) PANI:PEG (10 wt% PANI).
Figure 5-5a and Figure 5-5b show the topographical structure of the pure NaAlg film and the PANI:NaAlg film with 10 wt% PANI respectively. The structures are similar, with no significant changes to the macrostructure. These images show the polymeric structure of the NaAlg films as amorphous 'clusters' of polymers associated together, rather than the clear chains seen for the PEG. Polymer associations via entanglements and -OH groups are the primary sources of inter-chain interactions for NaAlg.²³ These images suggest it is the disruption of these inter-polymer interactions, as described in the FTIR section, which are the driving force behind the decreasing cohesive strength with no structural changes enhancing these effects further. On the other hand, the PEG films change their topography significantly when PANI is incorporated into the films. As seen in Figure 5-5c to Figure 5-5d the polymer goes from a highly ordered, crystalline structure to a more randomised, amorphous one. This change in polymeric structure could be the main reason for the cohesive strength changes observed in Table 5-2. Unlike NaAlg, the PEG is not a fully amorphous polymer, even when PANI is present, still exhibiting a degree of order. This could lead to multiple new, but weak, interactions between the amorphous and crystalline regions causing a net increase in the cohesion of the material, before additional PANI (up to 20 wt%) disrupts these weaker bonds resulting in a drastic decrease in cohesive strength.

5.2.5 Thermal Characterisation

The thermal stability of these polymer systems is a significant property to identify due to the fact that batteries are exposed to a wide temperature range during use and all components need to be stable, not undergoing any thermal decomposition. Quantifying any changes to thermal stability as a result of PANI addition is therefore essential to ensure these systems are suitable as binder materials. The DSC is used to show the first thermal transition when the films were heated between 25°C and 500°C and a full characterisation using DSC and TGA, including % mass loss and enthalpy changes was also carried out. **Figure 5-6** shows the DSC curves relating to the thermal stability of the films, based on the first transition and **Table 5-4** gives the full thermal characterisation of these films, with transitions relating to PANI being identified based on the previous study into PANI blend films.⁷



Figure 5-6: DSC showing how the thermal stability of a) PANI:NaAlg films and b) PANI:PEG films are changed when PANI content is increased, by observing changes to the position of thermal transitions with PANI content. Curves are also compared to a PANI, PVDF, CMC/SBR, NaAlg and PEG reference sample where appropriate.

Films created with both NaAlg and PEG showed a reduction in thermal stability as PANI is added. This is shown by the reduction in the onset temperature of the first thermal transition, from 50.85°C to 32.16°C, and 58.74°C to 31.83°C for NaAlg and PEG respectively. In both cases this initial peak has been attributed to the loss of moisture and associated water from the polymers as well as the melting of the polymers.^{23,27} This shows that thermal transitions can occur for these polymer systems within temperature windows that overlap with battery operating temperatures. While these transitions seem to be

mostly moisture loss, it can still lead to rearrangement reactions that could compromise mechanical stability and melting transitions can also occur to a similar effect. However, it should be noted that in the case of NaAlg this initial peak is broad and polymer melting occurs at much higher temperatures than the onset temperature, outside the battery operating temperatures. It is assumed that the disruption of the base polymer-polymer interactions by PANI, as seen in the previous experiments, is the reason for this reduction in thermal stability.

From the full thermal characterisation data in Table 5-4 the enthalpy requirements for this first thermal transition can be observed. Their magnitudes reduce significantly when PANI is incorporated, going from -302.08 J g⁻¹ to -190.49 J g⁻¹ for NaAlg and -155.93 J g⁻¹ to -107.79 J g⁻¹ for PEG. It is thought that the previous data shown in the analysis of these polymer films explains why less energy is required to liberate the water molecules and begin decomposition of the polymers. For instance, the reduction in the cohesive strength of the films and the changes to the polymeric structure of the PEG films seen in AFM. This data also seems to support the idea of the 10 wt% PANI:PEG film forming numerous weaker polymer-polymer interactions between amorphous and crystalline regions that can retain a cohesive strength comparable to the pure PEG film. This is seen by the retention in onset temperature for the initial thermal transition as you go from the PEG reference to the 10 wt% PANI film, while the subsequent peaks relating to the full decomposition still require temperatures much lower than the reference material, due to the fact the bonds formed are still weaker than the fully crystalline material. Additionally, this data also shows that PANI content leads to a small reduction in the onset temperature of the initial NaAlg decomposition, which is thought to be brought about via a similar means to that of PEG, however, as NaAlg is already amorphous prior to PANI addition, the effect on decomposition temperature is reduced. As stated above this reduction in the thermal stability of the polymers is concerning as all values fall within standard battery operating temperatures and are around room temperature. A proof-of-concept study, to incorporate these polymers into electrode materials will be done to determine whether they can bind electrode components and benefit cell electrochemistry relative to electrodes using the pure polymers and show the feasibility in this blending technique, using PANI, which could lead to possible future work to optimise base-polymer choice to improve the limited thermal stability.

Table 5-4: Summary of key thermal transitions for the PANI polymer blend films made with NaAlg and PEG as well as PANI, NaAlg and PEG reference samples. Data was acquired by using TGA and DSC techniques at a heating rate of 5 K min⁻¹. Numbers given in brackets are the standard deviations obtained from conducting these experiments in triplicate.

Base Polymer	PANI wt%	Key Thermal Transition	Onset Temperature (°C)	Mass Loss (%)	Enthalpy Change (J g ⁻¹)
PANI	Reference	Moisture Loss	50.2 (1.9)	4.33 (0.04)	-87.8 (2.2)
		Loss of Bound Molecules	201.5 (1.9)	4.14 (0.22)	-6.00 (0.68)
		Decomposition of Counter Anion	258.9 (0.4)	12.9 (2.6)	23.4 (0.9)
		Decomposition of PANI Backbone	291.7 (3.7)	25.5 (2.8)	-101.8 (10.0)
NaAlg	Reference	Loss of Bound Water/Melting	50.8 (0.8)	12.0 (0.1)	-302.1 (20.4)
		NaAlg Decomposition	212.6 (0.1)	45.4 (0.5)	256.7 (27.8)
NaAlg	10	Loss of Bound Water/Melting	37.4 (0.4)	6.74 (0.08)	-187.8 (5.7)
		NaAlg Decomposition	198.3 (0.1)	13.7 (0.2)	13.2 (1.2)
		NaAlg and PANI Decomposition	224.6 (0.9)	14.6 (0.5)	114.2 (11.6)
NaAlg	20	Loss of Bound Water/Melting	32.2 (0.6)	10.1 (0.3)	-190.5 (2.4)
		NaAlg Decomposition	201.9 (3.3)	12.6 (0.7)	6.34 (1.13)
		NaAlg and PANI Decomposition	228.7 (4.7)	11.5 (0.5)	75.2 (3.9)
PEG	Reference	Moisture Loss/Melting	58.7 (0.2)	-	-155.9 (0.1)
		Decomposition of PEG	368.3 (2.0)	92.4 (1.0)	-95.0 (11.9)
PEG	10	Moisture Loss/Melting	58.4 (1.9)	-	-128.4 (4.9)
		PEG and PANI Decomposition	242.7 (1.7)	85.3 (1.2)	-
PEG	20	Moisture Loss/Melting	31.8 (0.7)	1.66 (0.05)	-107.8 (0.5)
		PEG and PANI Decomposition	251.5 (2.5)	68.5 (2.1)	-

5.3 <u>Morphology and mechanical stability of anodes using PANI blends</u>

During characterisation of the films, it was theorised that these polymers may be insufficient at adhering the electrode components together and fail to make an electrode. After preparation, it was seen that PANI:NaAlg binder systems, were able to formulate electrodes, whereas the PANI:PEG binders did not. After drying, the graphite naturally delaminated with very little effort, showing insufficient adhesion. Additionally, because the graphite was only delaminating in a fine powder, rather than larger flakes, it implies that these electrodes were also not cohesive meaning these PANI:PEG polymers were unsuccessful at binding any of the electrode components together. Therefore, only the PANI:NaAlg electrodes will be assessed going forward.

5.3.1 *Morphology*

SEM images showing the morphology of the anodes created using the PANI:NaAlg binder systems is given in **Figure 5-7**. The anodic morphology remains unchanged compared to the other anodes discussed in chapter 3. Additionally, the binder is located the same location to that of the commercial binders (PVDF and CMC/SBR) and NaAlg, with the polymer being situated towards the edge planes of the graphite and the interstitial sites between the particles.²⁸ This is a function of the hydrophilic nature of the NaAlg compared to the hydrophobic graphite, reducing the capacity for interactions between the two.

While the introduction of PANI has a minimal effect on the overall morphology and the location of the binder remains largely the same, there does seem to be an apparent increase in the amount of dispersed 'free' polymer upon the graphite particle surfaces relative to the NaAlg SEM images (**Figure 5-7c**). This indicates that there is a greater interaction between the polymeric regions and the hydrophobic graphite, which is thought to be related to the hydrophobicity of the added PANI. This property can be altered when PANI is in different forms, for example, in the ES form the material is hydrophilic whereas, the EB form becomes hydrophobic.²⁹ The previous FTIR data of the PANI films implied that interactions between the PANI and base polymers could be occurring via the polarons of the PANI backbone. This results in the polymer more hydrophobic and could lead interactions between the hydrophobic basal planes of the graphite and the polymer system, dispersing more the binder across the entire electrode surface. However, it should be noted that, the bulk of the polymer is still hydrophilic with the majority of the binder still being observed between graphite particles at the edge planes. It is argued here that the addition of PANI gives the binders an amphiphilic in nature similar to gelatin in chapter 3, albeit to a lesser extent.³⁰





Figure 5-7: Scanning electron microscopy images of graphite electrodes made using PANI:NaAlg binder systems, all images were taken at an excitation voltage of 10kV. a) PANI:NaAlg (10% PANI) and b) PANI:NaAlg (20% PANI). c) shows a NaAlg reference image for comparison (from chapter 3).

In addition to the SEM images, AFM was also conducted, with topography and modulus scanning being carried out due to the modulus differences between the graphite particles and the polymer. The scans were used to visualise the surface further and reinforce the conclusions made from the SEM images on the polymer location.²⁵ These images are shown for both the 10 wt% and 20 wt% PANI systems in **Figure 5-8**. In this instance the modulus scans, **Figure 5-8b** and **Figure 5-8d** show the softer polymeric regions in darker colours, with the harder graphite particles as lighter areas. The images support what was seen with the SEM images, with the majority of the polymer regions situated at the edges of graphite particles, with a degree of dispersed polymer deposited

onto the graphite particles. It is hard to quantify whether there is an increased amount of free polymer dispersion in AFM due to the limited area that can be analysed, but these images do seem to support the SEM images across this scan area.



Figure 5-8: AFM imaging of the graphite electrodes created using the PANI:NaAlg binders. a) PANI:NaAlg 10% topography, b) PANI:NaAlg 10% modulus scan, c) PANI:NaAlg 20% topography and d) PANI:NaAlg 20% modulus scan.

However, there is an interesting change between the AFM modulus images shown in **Figure 5-8** and those found for the DES-modified NaAlg from chapter 3 (**Figure 3-8**). In the previous images the NaAlg polymeric regions did not show resolved CB particles, indicating weaker interactions between the NaAlg and the carbon black (CB) due to the purely hydrophilic nature of the polymer. On the other hand, the gelatin samples, which were amphiphilic, showed resolved CB particles as the presence of both hydrophilic and hydrophobic groups allowed the polymer to interact with and 'wet' the CB.²⁶ The resolution of the CB particles in the PANI:NaAlg polymer regions further support the idea that these polymers are made amphiphilic in nature by the PANI and are capable of further interactions between the hydrophobic carbon components of the anode.

5.3.2 Mechanical characterisation

The adhesive strength of these materials was determined using the critical load methodology discussed in chapter 3, where the load required to break apart the active material from the copper current collector is denoted as the adhesive strength. The data acquired for anodes using the PANI polymer blends is given in **Table 5-5** along with pure NaAlg, PVDF and CMC/SBR reference samples, which use the same values as seen in **Table 3-3**.

 Table 5-5: Scratch test data showing the critical load of the anodes created using the

 PANI:NaAlg polymer blend as a binder at 10% and 20% PANI content. Additionally,

 reference data for pure NaAlg, PVDF and CMC/SBR are also given.

PANI Blend	Critical Load (N)	% Difference in Critical Load
PVDF Reference	3.59 (0.29)	-
CMC/SBR Reference	3.29 (0.10)	-
NaAlg Reference	4.19 (0.31)	-
PANI:NaAlg (10 wt% PANI)	3.28 (0.16)	- 21.7 %
PANI:NaAlg (20 wt% PANI)	2.03 (0.17)	- 51.5 %

The data shown in **Table 5-5** shows that the addition of PANI significantly reduces the mechanical stability and adhesion of the electrodes. There is a greater reduction in critical load for the anodes compared to the polymer films. This is notable as it shows that despite the increased interaction between the binders and the hydrophobic components, it does not translate to improved adhesion. It is thought that the inherent brittleness of PANI and the aforementioned disruption to polymer-polymer interactions, caused by PANI, that is responsible for the reduced adhesive strength. While this reduction in adhesive strength is significant, with a 20 wt% addition of PANI halving the adhesive strength of the anode, it should be noted that the 10 wt% PANI sample possesses a critical load (3.28 N) similar to that of both CMC/SBR (3.29 N) and PVDF (3.59 N) references. This implies that the 10 wt% PANI binder has a comparable mechanical stability to the commercial reference binder and thus should be applicable in LIB anodes. Therefore, the 10 wt% PANI anodes were incorporated into half cells and tested to determine whether the presence of PANI provides an electrochemical performance enhancement as this could determine whether these PANI blends are a viable binder in LIBs.

5.4 Electrochemical characterisation of anodes using PANI blends

Electrochemical characterisation carried out is identical to the testing done in chapter 4 on the DES-modified gelatin and NaAlg binders and the remanufactured graphite materials. It should be noted that the reference data used here for NaAlg, PVDF and CMC/SBR is from chapter 4, with the NaAlg reference being taken from the data denoted as NaAlg 100:0.

5.4.1 Formation cycling

The aim of formation cycling is to establish an SEI layer upon the anodic surface and to ensure that lithium intercalation is occurring. As was the case in chapter 4, these processes can be confirmed by looking at the capacities, coulombic efficiency, and voltage profiles of these cells. As stated in the previous chapter, SEI growth is essential for continued battery stability as it limits electrolyte decomposition and forms a layer that can only be passed through by unsolvated lithium ions, thus removing the risk of graphite exfoliation. A key way to show that SEI formation has occurred is by comparing coulombic efficiency on the 1st and 5th cycle, as the formation of an SEI layer will minimise capacity losses associated with electrolyte decomposition. The coulombic efficiency data is shown in **Table 5-6** along with the average capacity data. Similarly to the reference samples, the cells using PANI:NaAlg as the binder showed an expected increase in coulombic efficiency from cycle 1 to cycle 5 and in the voltage profiles of these cycles (**Figure 5-9**) the feature related to electrolyte decomposition, labelled 'ED', is missing in cycle 5. **Table 5-6:** Average charge/discharge capacities for the lithium half-cells using graphite anodes with PANI:NaAlg (10 wt% PANI) as the binder compared to references anodes using PVDF, CMC/SBR and NaAlg. Charging refers to intercalation of lithium into graphite and discharge refers to deintercalation of graphite.

Binder	Cycle Number	Average Charge Capacity (mAh.g ⁻¹)	Average Discharge Capacity (mAh.g ⁻¹)	Average Coulombic Efficiency (%)
PVDF Reference	1	295 (25)	251 (20)	85.5 (1.1)
	5	305 (9)	295 (13)	96.6 (1.6)
CMC/SBR Reference	1	294 (27)	263 (21)	86.6 (1.2)
	5	302 (3)	289 (8)	95.9 (2.6)
NaAlg Reference	1	320 (20)	284 (17)	88.8 (0.2)
	5	315 (8)	307 (11)	97.2 (1.0)
PANI:NaAlg (10 wt% PANI)	1	279 (24)	246 (26)	87.9 (2.4)
	5	303 (2)	301 (2)	99.3 (0.1)

However, it should be noted that the coulombic efficiency of the PANI cells is much higher than the other anodes after the initial cycle, achieving efficiencies > 99%. As stated in chapter 4, this is the expected efficiency of a LIB, but the fact that the anodes using the conventional PVDF and CMC/SBR binders cannot achieve such efficiency implies that this inflated efficiency is related to side reactions across the electrode-electrolyte interface brought about by the inclusion of PANI in the binder. These could include electron exchanges across the interface during the migration of polarons during cycling or an interaction between PANI and the lithium ions themselves. Interactions between PANI and lithium have been documented previously. Lithium ions are capable of coordinating to imine (C=N⁺) groups within emeraldine base forms of PANI.^{31–33} Some of these lithium-doped PANI compounds, sometimes referred to as lithium emeraldinate, have been explored as an active materials in aqueous LIBs and are shown to possess reversible redox chemistry.³³ As imine groups will also be available in these polymer blends, with the FTIR data indicating an increased availability of these groups, lithium doping of PANI is anticipated to be the main source of the improved efficiency of these anodes versus the reference cells.

Evidence of such side reactions can also be seen in the voltage profiles in **Figure 5-9**. During cycle 1 multiple plateaus can be observed between two of the lithium intercalation steps shown in **Figure 4-1**, step 4 and step 3. These steps are not observed for any other anode material detailed in this project and is thought to be related to side reactions with PANI to create lithium emeraldinate. The previous study into this form of PANI showed that EB PANI needs to be doped with lithium and subsequently deprotonated with a lithiated base to create lithium emeraldinate. It is proposed that these initial reactions are responsible for the additional steps in cycle 1. Where, lithium ions dope PANI during initial intercalation, then lithium carbonate species, formed by electrolyte decomposition, deprotonate the lithium-doped PANI to form lithium emeraldinate.³³ While similar reactions will occur throughout battery cycling, due to the reversible redox nature of lithium emeraldinate, it is thought that the relatively low PANI content in the anodes and the limited electrolyte decomposition in subsequent cycles contribute to these steps being no longer visible.



Figure 5-9: Voltage profiles (at 0.1C rate) for the half-cell formation cycles of a graphite anode using the PANI:NaAlg (10% PANI) polymer blend as the binder. Solid lines are the 'charging' curves and the dashed lines are the 'discharging' curves in relation to graphite.

It is interesting to note however, that despite the evidence of additional redox chemistry within the anode materials using PANI:NaAlg binders this does not translate to elevated capacities. As seen in **Table 5-6** where the average capacities are consistent with those of the reference anodes using conventional binders and pure NaAlg. While the fact that the use of these binders does not hinder capacity performance is a positive outcome, it is thought that because the binder is also capable of possessing capacity that these values would be larger overall. It is possible that these contributions are factored in and as a result of using these binders, lithium is not intercalating as efficiently into the graphite active material. Alternatively, the potential interactions with SEI components such as lithium carbonate could be affecting stability of the SEI, and subsequently the graphite anode, with structural defects causing capacity fade. It is unclear at present, which effect is responsible, or if such an adverse effect is taking place. Rate tests were conducted in order to show cell capacities and stability at high cycling rates, which should show if any capacity fading mechanism is occurring.

5.4.2 Rate testing

Analysing the rate dependency of cell performance is essential when considering alternative battery components. Rate testing was carried out in the same way as chapter 4 in order to characterise the performance of these anode materials, the results are shown in the waterfall plot in **Figure 5-10**. Where the capacity at cycling rates of 0.1C and 0.2C is almost identical with little deviation, before a 10% loss (~ 30 mAh.g⁻¹) is seen at 0.5C and a 33 % loss (~ 100 mAh.g⁻¹) is seen at 1C before the capacity significantly decreases to ~ 20 mAh.g⁻¹ at 5C. This general behaviour is similar to that seen for the DES-modified NaAlg samples shown in **Figure 4-3**, except the magnitude of the capacity losses are slightly higher for the PANI:NaAlg samples. Though this is not believed to be significant and is likely brought about by environmental factors, such as external temperatures.

As stated previously the substantial reduction in graphite capacity when cycling cells at C-rates > 1C is not fully understood but has been attributed to multiple factors such as temperature, particle morphology, anodic surface area and lithium intercalation rates. For instance, there are numerous rate determining steps and phenomena that occur during the different stages of lithium intercalation that will significantly limit the capacity reached at high C-rates. These include steps such as the desolvation of lithium from electrolyte solvent species at the SEI surface prior to intercalation, irregular propagation of lithiation throughout graphite particles and deviations in lithium-ion diffusion coefficients brought about by 'liquid-like' and 'fully lithiated' stages of intercalation (i.e. 1L and 1, seen in **Figure 4-1**).^{34–37} Together, these effects contribute to the poor intercalation of lithium and subsequent low capacity at 5C, which is then regenerated when the C-rates are lowered to 1C and below.

Whilst the majority of the capacity lost at high C-rates is regenerated when low C-rate cycling (0.1C and 1C) is repeated after cycling at 5C, as seen in cycles 25-35 in **Figure 5-10**, a ~10% reduction in both charge and discharge capacities is observed. A previous investigation into improving graphite rate capabilities showed similar behaviour to that seen here, with a reduction in overall capacity at the same C-rate before and after rate testing.³⁸ It can be concluded that this data seems typical of that of a graphite half-cell and behaves consistently with the samples analysed in chapter 4, with the addition of PANI to the binder seemingly having minimal impact on the rate capability of the cells. At this point the only effect PANI seems to have on electrochemical performance is on

the coulombic efficiency, which is predicted to be due to side reactions rather than improved stability limiting electrolyte decomposition. Additionally, there is no clear improvement to capacity and rate capability showing that the improved conductivity seen at the beginning of the chapter cannot be translated to improved cycling performance with the present samples. Impedance testing was carried out to determine whether the presence of PANI led to any decreases in impedance contributors relative to the reference samples from chapter 4.



Figure 5-10: Waterfall plot showing the capacity of a lithium half-cell with a graphite anode using a PANI:NaAlg (10 wt% PANI) binder system. Black shows the charging capacity of graphite and red outlines show discharge capacity.

5.4.3 *Electrochemical impedance spectroscopy*

As with chapter 4, the EIS data obtained from these cells were modelled relative to the Randles circuit given in **Figure 4-7a**. The analysis of the Nyquist plots, shown in **Figure 5-11**, was based on similar EIS experiments from literature investigating the effect of novel binders in LIBs.³⁹ Therefore, the impedance contributors were defined in a similar manner; R_S – resistance of the cell components, electrode and electrolyte, R_{SEI} – resistance of the SEI layer and R_{CT} – charge transfer resistance across the electrode-electrolyte interface. The modelled resistance values for each contributor for the half-cells using PANI:NaAlg in the anodes after formation cycling and after the rate test are given in **Table 5-7** along with reference samples for PVDF, CMC/SBR and NaAlg from chapter

4. It should be noted that, similarly to the data shown in chapter 4, the Nyquist plots for this half-cell system are significantly flattened, as seen in the y-axis used in **Figure 5-11**, which is indicative of the porous graphitic surface of the anode.



Figure 5-11: Nyquist Plots after formation and rate testing to show how impedance changes with regards to each interfacial region. Data was obtained at 0.1V, between 300,000 Hz and 0.1 Hz. Data fit shown with blue lines.

The Rs values for these PANI:NaAlg cells are similar in both magnitude and behaviour to that of NaAlg, which is reasonable due to the similarities in these anode systems and that NaAlg is still the dominant binder in PANI:NaAlg. The most notable difference in the impedance data for the PANI:NaAlg samples versus the reference cells is the notable reduction in R_{SEI} and R_{CT} after the rate testing. Generally, this indicates that charge transfer between the electrode and the electrolyte is easier in these PANI:NaAlg systems after excessive cycling compared to the reference scenarios. In most instances, the thickness of the SEI grows during cycling as more electrolyte decomposes at the electrode surface, albeit at a limited rate due to the SEI presence, which increases R_{SEI} over time. It is assumed in these systems that the thickness of the SEI stays relatively consistent over the course of the rate test. Instead, it is thought that the possible interactions between SEI components, such as lithium carbonate, and PANI to form lithium emeraldinate may be the source of the reduction in R_{SEI} . As the greater interconnectivity between the electrode and SEI layer could be improving the movement of charge between the two components and establishing more electroactive forms of

lithium within the SEI layer could shorten the diffusion pathway for these ions. This is also observed in the reduced Warburg element for the PANI:NaAlg cells compared to all of the reference cells (~ $4 \times 10^{-1} \Omega$.s^{-0.5} versus ~ $5 \times 10^{-1} \Omega$.s^{-0.5} for NaAlg and ~ $7 \times 10^{-1} \Omega$.s^{-0.5} for PVDF), corresponding to lower diffusion resistance. Regardless of whether this effect is the source of this impedance decrease or not, the retention of coulombic efficiency throughout the rate test implies that it is not a function of a thin, unstable SEI layer. Additionally, the formation of this more conducting SEI layer could be the source of the reduced R_{CT} as it may facilitate easier charge transfer across the electrodeelectrolyte interface. A similar effect was observed in electrodes using PEDOT:PSS binders, with additives such as glycerol or CMC, where the R_{CT} values were 7 times lower than commercial electrodes due to the presence of these interconnected conducting binder systems.^{40,41}

While it should be noted that these reductions in interfacial resistances are not causing an improvement in capacitive performance of these anodes, the reduction in impedance and the higher coulombic efficiency imply these cells are more conductive and electrochemically stable compared to the reference half-cells. Therefore, it does seem that the addition of PANI to the NaAlg binder has succeeded in its intended purpose of improving some of the electrochemical characteristics. However, a lack of capacity enhancements as well as the aforementioned mechanical and thermal stability issues does limit the viability of these PANI:NaAlg binders in further application. Investigations into other, similar polymer blends may yield a more viable binder, which can retain the benefits observed in this section and improve upon the limitations discussed previously.

 Table 5-7: Modelled EIS resistance data for the Nyquist plots shown in Figure 5-11,

 using the Randles circuit given in Figure 4-7a. EIS measured after the initial

 formation cycles and after rate testing. The values presented are using the circuit that

 models the EIS response best. Errors in fits are given in brackets.

	R_S/Ω		R_{SEI}/Ω		R_{CT}/Ω	
PANI Blend	Formation	Rate Test	Formation	Rate Test	Formation	Rate Test
PVDF	3.92	4.73	5.68	8.46	8.25	7.42
	(0.03)	(0.12)	(0.06)	(0.16)	(0.08)	(0.07)
CMC/SBR	4.16 (0.04)	10.5 (0.1)	7.32 (0.23)	8.06 (0.19)	13.4 (0.3)	8.98 (0.16)
NaAlg	1.85	3.26	1.40	4.08	5.12	5.07
	(0.01)	(0.03)	(0.06)	(0.08)	(0.05)	(<i>0.06</i>)
PANI:NaAlg	2.26	3.36	4.95	3.51	6.67	3.65
(10% PANI)	(0.01)	(0.06)	(0.19)	(0.18)	(0.19)	(0.15)

5.5 <u>Recyclability study using ultrasound</u>

The main aim of formulating these PANI polymer blends was to develop binder systems capable of enhanced performance, while also ensuring they still provide a simple delamination route with ultrasound and water, hence the use of water miscible base polymers. **Figure 5-12** shows the images before and after processing using an ultrasonic bath setup also used for the NaAlg-based systems in chapter 3. This lead to an identical scenario to those previous experiments where full delamination was possible within just a few seconds.²⁶ As with the previous NaAlg-based systems, it is predicted that the water is able to break the adhesive bonds with the ultrasound acting as a catalyst. PANI content does not seem to impede this, and based on the mechanical stability data, it is assumed it would improve the rate of this separation due to the weaker adhesive bonds, keeping the electrode together. However, this effect is negligible in this polymer blend system due to the already efficient nature of the delamination when NaAlg is used. It is possible that

with another base polymer, one that is more stable in water, this effect could be used to streamline the delamination process via this low-powered ultrasound route.



Figure 5-12: Images showing the electrode materials created using the PANI:NaAlg (10% PANI) polymer blends as the binder before (a) and after (b) the use of water and a low power ultrasonic bath (power intensity $\approx 0.02 \text{ W cm}^{-2}$) for delamination.

5.6 <u>Conclusions</u>

This chapter has showed that the polymer blend methodology outlined in a previous study can be utilised to form PANI polymer blends with different water miscible polymers that may present a new kind of LIB binder. Analysis of polymer films using PANI and NaAlg or PEG showed improved conductivity over films solely utilising these water miscible polymers, which was increased further when a larger concentration of PANI was used up to 20 wt%. However, thermal and mechanical stability was diminished with PANI content, indicating that a compromise in PANI composition would be required in order to form effective binder systems. In fact, formulation of anodes using the PANI blends found that only the PANI:NaAlg (10 wt% PANI) system was able to create an electrode coating that was adhered to the current collector. Characterisation of the electrode created with this binder found that, as predicted, the mechanical stability was decreased compared to an anode using NaAlg as the binder. Electrochemical characterisation found evidence of additional side reactions occurring during cell cycling, which was attributed to the formation of lithium emeraldinate, a lithiated form of PANI capable of reversible redox reactions, which may be contributing to the higher coulombic efficiency of these cells versus references using PVDF, CMC/SBR and NaAlg as the binders. This was also evidenced in EIS were the R_{SEI} and R_{CT} values are reduced in the cells using PANI:NaAlg after rate testing. This was attributed to a shortened diffusion pathway for lithium ions due to the formation of these lithiated forms of PANI during

initial cycling by interactions between PANI and the SEI components, such as lithium carbonate. However, the capacity of cells using these PANI binders was not improved compared to the reference scenarios. This chapter has shown that the concept of using polymer blends with PANI and water miscible polymers such as NaAlg can provide benefits to the battery materials during cycling, but this comes at the cost of mechanical and thermal stability. Further development into this kind of binder system may identify optimal polymers and PANI compositions to allow for the electrochemical benefits while limiting stability limitations and possibly allowing for improvements to capacity. Future work would also investigate applying this type of binder into cathode materials. Finding blends that can be dissolved in solvents other than water for manufacturing, to avoid cathode cracking and lithium leaching, but can then be susceptible to water-based delamination techniques like the ultrasound methodology outlined in this chapter.

5.7 <u>References</u>

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Chapter 6: Designing lithium-ion batteries for recycle: Alternative cell designs and adhesives¹

6.1 Introduction

The usage of alternative adhesives has been shown in previous chapters to present easier routes to delamination and facilitate separation of different electrode components. Alternative extracellular adhesives also present a route for simpler disassembly of lithium-ion batteries (LIBs) prior to electrode delamination. Currently, there are multiple joining methods used to connect cells together to form battery packs for structural integrity, strength and electrical continuity. These joining methods can either be physical (clips, screws, springs etc.), metallic (welds and solders), inorganic cements or organic adhesives. Unfortunately, the properties needed during use are generally at odds with the end-of-life (EOL) requirements. In use the joint needs to be durable and non-reactive whereas at EOL it needs to be soluble or reactive. Most recycling processes start with a disassembly of the battery pack down to either module or cell level. From there, most physical and hydrometallurgical recovery start with comminution (shredding) to break joints and separate the different phases which results in cross-contamination between components and results in low value product streams. Dismantling the cell down into individual electrode materials as an alternative to shredding, can significantly improve economics and product purity but it is hampered by the complexity of the component joining techniques.²

Previous studies investigating the economics of disassembly processes for commercial LIBs showed that economic recycling of battery packs requires automation to be economically viable.^{3,4} Automated industrial disassembly has been argued to be a key enabler of a circular economy of electric vehicle batteries.² However, automation is limited by current pack, module and cell designs. While the primary concern of battery design is to ensure safe and long battery performance with a high-power density to efficiently store electrical energy, current designs make disassembly complex due to the array of connectors used, the scale and packing of the cells and mechanical and chemical damage to the components during use.^{5,6} It was noted in particular that the biggest barriers to disassembly were the number of screws when disassembling from pack to module and the number of welds and structural adhesives as well as the number of modules when going down

to cell level. **Figure 6-1** shows some of the locations and application for polymeric adhesives used for in battery packs. For the structural and longevity reasons listed above, thermoset resins and unreactive fluorinated polymers have been extensively used throughout battery structure, like the fluorinated polyvinylidene fluoride (PVDF) binders present within the electrodes.



Figure 6-1: Examples of where structural adhesives are used within a battery pack using cylindrical cells

Technoeconomic assessments comparing shredding and disassembly of LIBs found that a cost saving during battery manufacturing (with respect to using virgin material) of up to 20% could be achieved using shredding whereas cell dismantling could recover material with up to 80% cost reduction.^{7,8} The advantages of shredding are that it rapidly reduces the active battery into a safer format and it is a process that is easily scaled, although the atmosphere around the shredder does need to be controlled. However, shredding does not separate aluminium from lithium metal oxide efficiently and attrition milling down to sub-mm scale is required to get reasonable separation.⁹ Studies have shown that impurities incorporated into recycled cathode material can significantly affect the performance of cells.¹⁰ Additionally, the majority of electrolyte cannot be recovered,

with high value components like LiPF₆ being lost, which can lead to other issues like the production of hydrofluoric acid (HF), and the necessary removal of organic solvent from wastewater streams. There are, however, caveats with these studies which, in most cases, have not considered the cost of disassembly and, for those which have, they do not dismantle beyond module level. The logistics of moving waste is also important and it was shown that reducing transport and disassembly was important to the overall economics of recycling.¹¹ The geospatial configuration of a future recycling system will have a bearing on the impacts that arise at the EOL. The scale of the recycling plant is also important as are the hazard classification of EOL cells as it will affect the transportation costs if they are classified as hazardous. The configuration of technologies used for EOL processing, will have a bearing on the topology and structure of this future industry. Simple pre-processing that can take place near to the point of disposal may aid in reducing the environmental burden of the EOL phase. Batteries that can be disassembled more easily close to point of disposal may unlock "hub and spoke" recycling models.

As well as economic benefits, previous life cycle analysis (LCA) shows that recycling processes have the potential to reduce greenhouse gas emissions of the entire battery life cycle by 20 kg CO₂eq/kWh bc.¹² While this industry will need to facilitate existing battery designs in EOL waste, in the future, better designed batteries could unlock enhanced and more efficient recycling methods, which will aim to achieve the economic and environmental benefits outlined above. A comprehensive roadmap for LIB recycling, summarises the key developments in LIB recycling, including design for recycle, and issues that still need to be addressed to establish a scalable recycling methodology capable of establishing a circular economy.¹³ While an important aspect of these methodologies will include alternative electrode binders like those discussed in the bulk of the investigation detailed in this thesis. This chapter demonstrates some simple design modifications that could be adopted to improve the ease of pack disassembly. Dummy cells and modules were used to show the efficiency of disassembly using robotics and, where appropriate, times are compared to the time taken for commercial cells to be dismantled as proposed by Lander et al.⁴ An environmental impact study of making these design changes, compared to a Nissan leaf reference scenario taken from Lander et al. is then detailed, along with a similar study comparing the delamination of electrodes using alternative, sodium alginate (NaAlg), binders and commercial electrodes using ultrasonication.4,14,15

6.2 <u>Proposed cell conformation and adhesive changes</u>

Returning any device to its constituent components is fundamentally restricted by the numbers of interfaces and the methods chosen to join those interfaces. Recycling is made more challenging when dissimilar materials with incompatible properties are joined permanently using non-reversible adhesive bonds, making them difficult to separate. The three basic joining approaches; thermal welding, chemical adhesion and physical connection have implications for the cost, speed and permanency of the join and its subsequent release. The complexity of battery architectures has been highlighted previously.^{1, 15, 19} There are numerous aspects of pack, module and cell design which can be adopted for simplified disassembly and recycling:

- Minimal use of thermoset adhesives
- Fewer, but larger cells
- Fewer fixing types
- Cells that are more easily opened
- Electrode binders that can be fully dispersed using water.

6.2.1 Redesigned 'zigzag' cell conformation

Disassembly tends to lend itself to cell configurations with larger amounts of battery material per cell, i.e. prismatic and pouch rather than cylindrical. This is for two main reasons: the time taken to open the individual cells and the mechanical separation of cells from each other in the module. The Tesla Model S P85 battery pack, for example, has 16 modules, containing a total of 7104 cells whereas the BMW i3 Mk 1 has 8 modules, each containing 12 cells (96 in total). Cell opening is viable with the latter as each cell opening process yields approximately 2 kg of material but with the former, less than 50 g of material are obtained. The disassembly of cylindrical cells is further complicated by their geometry, with active materials, foils and separators being spiral wound into a "swiss roll" like configuration, rather than the planar geometry of electrodes in pouch and prismatic cells.

In most pack and module designs currently used in the automotive sector, structural adhesives provide rigidity and strength to the assembly. Their use is logical, as they are inexpensive to apply and irreversibly provide the strength needed to minimise movement of cells during use. Most of the adhesives used are thermosets, based commonly on epoxides or polyurethanes. Debondable adhesives have also been explored, which incorporate an element which enable depolymerisation or bulk delamination, however, numerous difficulties have been identified with using heat, light or electrical potential as debonding stimuli in a battery pack.¹⁶

An important factor in the cost of LIB recycling is the complexity of pack disassembly. Manual disassembly is too slow and costly in many regions due to labour costs. It has recently been estimated that the manual disassembly time for many makes of electric vehicles are currently in the range 8-10 h. Automated pack disassembly down to modular level has been estimated to take 1-2 h and this is severely limited by the retooling of robots and the time taken to remove welds and glues. Most fixing methods are permanent, so servicing and EOL are not part of the pack design. Nine joining methods for metals in batteries have recently been identified,¹⁷ and of these, only mechanical assembly (screws and clips) is seen as a process which makes disassembly easier, however mechanical fixtures add to the weight of the battery pack. An important design for disassembly would be to limit the use of structural adhesives and provide strength to the module or pack by alternative methods. One way this could be achieved is to create a permanent link between pouch or prismatic cells and strategically place only a small amount of adhesive at a point where selected directional movement could physically break the bond. One such arrangement could involve hinging the cells at alternate ends to create a zigzag conformation as shown in Figure **6-2**. This decreases the degrees of freedom that each cell can independently move in and generates levers between the cells. This could significantly decrease the amount of adhesive that needs to be applied to impart structural rigidity. If the properties of the adhesive are tuned correctly, separation of the cells into a linear configuration (Figure 6-2) could be carried out effectively with programmed robots as only a simple extension of the design is required in the x-axis for the disassembly to occur.



b)



Figure 6-2: The proposed zigzag conformation for pouch cells. a) image of the dummy cell used in these experiments and b) the schematic diagram for the conformation showing placement of the adhesives.

6.2.2 Alternative extracellular adhesives

Pressure sensitive adhesives (PSAs) were used in this study as alternatives to the thermoset resins currently used to formulate the packs and modules of LIBs. PSAs are a versatile class of viscoelastic materials which form bonds using initial pressure and flow, unlike conventional adhesives, which bond once they have hardened through a chemical or physical process. PSAs do not require additional agents such as heat, water, or solvents to activate. Due to this, the rheological

properties of the adhesive must be adjusted specifically to their application.¹⁸ The three main characteristics to be considered are ultimate adhesion, shear resistance and initial tack. Ultimate adhesion is the measure of the strength of the fully formed bond once the adhesive has set, shear resistance correlates to the adhesive resisting forces parallel to its surface and initial tack corresponds to the property that controls the instantaneous formation between the adhesive and adherend.¹⁹ Contact adhesives are easier to apply than thermoset resins and are already used in small aspects of pack construction, their application over large surface areas make debonding slow and necessitates large volumes of solvents.

An investigation was carried out to compare the effectiveness of different types of commercially available PSAs including glue dots, double-sided tape, and Velcro. A peel test with tensile testing apparatus was used to simulate how a real module of cells using the proposed zigzag conformation would be pulled apart. For this investigation two pouch cells of total weight 1.6 kg were created with a hinge between them by heat sealing a large pouch (41.5 x 23.5 cm) in the middle. Initially no adhesive was used to set a base level for the different PSAs and to accurately compare their loading and extension which in turn corresponds to the energy required to break the connection. All adhesives were able to resist shearing motion in the z-axis and provided reasonable strength in the x and y axes as shown in **Table 6-1**.

Pressure Sensitive Adhesive	Average Load (N)	Maximum Load (N)	Energy Usage (J)
No Adhesive	6.02	9.76	2.12
Glue Dots	15.83	22.65	2.82
Velcro Strips	31.90	67.89	3.43
Double Sided Tape	58.67	103.77	4.49

Table 6-1: Comparison of the forces and associated energy required to open the modules using the zigzag conformation when different pressure sensitive adhesives are used.

As seen by the total energy usage it is clear that double-sided tape is the strongest adhesive of the set closely followed by Velcro. Both provide viable solutions to holding a zigzag configuration cell together, however weight and spacing must be considered alongside the ease of removal of adhesive. In contrast to glue dots or double-sided tape, using Velcro increased the thickness of the sample design by nearly 35 %, which would decrease the power density of a real LIB. Additionally, a weight calculation was carried out to evaluate each adhesive for the test sample (Table 6-2) as minimising weight is essential in automotive products such as electric vehicle batteries. It was found that Velcro contributes a relatively high amount of additional weight, while the glue dots contribute almost no weight. The removal of the adhesives themselves from the cells was also investigated to ensure that full separation of all components can be completed. This found that the double-sided tape was found to be the most difficult to remove, due to the sticky residue left behind. However, even this residue can be removed relatively easily with an acetone wash or by hand. Both Velcro and the glue dots did not leave residual material behind, thus making them a preferential choice in this respect as they would not require the additional removal step and therefore provide the simplest disassembly procedure. This is particularly useful in the area of pack or module repair and may decrease the proportion of cells being scrapped during production.

Pressure Sensitive Adhesive	Dimensions	Weight (g)	Average time taken to remove manually (s)
Glue Dot	0.3 cm radius	0.016	20
Velcro Strip	2 cm x 2 cm	0.434	25
Double Sided Tape	2 cm x 2 cm	0.052	50

Table 6-2: Physical properties of the pressure sensitive adhesives used in this study including the dimensions and weight of the adhesives and the time taken for removal.

6.2.3 Pack and cell opening procedure

To demonstrate the applicability of using these changes to the design and extracellular adhesives, the dummy battery pack, shown in Figure 6-2a, was constructed using 8 cells, each

scaled down to 110 x 140 mm weighing ~193 g each, which was about 20 % of the mass of a pouch cell that would be used in the Nissan Leaf. This was done due to limitations of the lifting capacity of the robots used in these tests. 'Franka Emika Research 3' robots were used to lift the 8-cell module from a box using two tabs. Two glue dots were adhered on alternate sides of the line of joined cells such that they could be aggregated into a zig-zag pattern. This approach enabled the ensemble to have mechanical strength but allowed some movement within the confines of the module container. The robot was able to lift the module contents and extend the string of cells into a straight line, as shown in **Figure 6-3**, in only 15 seconds and this can also be viewed in video format. This automatic process could resemble how industry standard disassembly of a full battery pack could take place.



Figure 6-3: Images showing the stages of robotic module opening when the zigzag cell conformation is used. This process takes place over the course of 15 seconds.

Alternative ways in which this could be carried out would be using strapping, commonly used in commodity transportation. These straps are usually made of polypropylene or polyester with either a thermal or metal crimped seal. This provides a physical join which is quicker to unfasten/refasten. Cutting this band would provide instantaneous cell release and simplify disassembly. Some test modules were made with single sided adhesive tape across the cell stack. These are reinforced tapes but allow quick release when the tape is cut. After the process outlined in Figure 6-3 the cells would be opened and the electrodes taken out and separated. Cell opening can be easily automated with mechanical processes, however the material composition of the cell container has a significant impact upon which method can be utilised. A list of different methodologies that can be used are given in **Table 6-3**. The pouch cells are laminates of aluminium with polyethylene terephthalate and polypropylene.²⁰ These are easily cut open with ceramic blades, leaving little residues or extra contamination. Other opening methods such as using lasers or plasma, produce heat during the cutting process, but this can be optimised through fast, short pulses allowing for heat dissipation.²¹ Any heat or sparks may ignite the flammable electrolyte. The sparking and heat removal may be further reduced with cooling fluids, which can also have a second benefit for passivation of the components as the cell is opened.²² In addition, ultrasound could be utilised for pouch cell opening, as this tool can cut through multi-layers, and is used for materials which melt if exposed to heat, such as the laminate.

Cell Opening Methods	Advantages/Disadvantages		
Ceramic Blade	Mechanical cutting with ceramic blades, is simple. However, the tooling parts may require replacing frequently which adds to the cost and any HF released from the cell will exacerbate wear considerably. Cutting fluids can be used to reduce wear, and to improve throughputs.		
Ultrasound	Suited to materials which cannot be exposed to heat, such as plastics which melt. Owing to lack of heat, this process may be the safest option for pouch cells.		
Plasma	Requires electrically conductive materials and is often used for metals. However, a significant level of heat is produced that would need to be dissipated during long-term usage.		
Laser	In most laser cutting applications, a robot is loading/unloading metal sheets to the bed of a laser cutting machine. Because lasers produce a large amount of heat, this could damage these robotics unless heat dissipation is carefully controlled.		
Water Jet	High pressure water jets can be used for a wide variety of materials but may react with or cause contamination of the products if mixed with abrasive ingredients.		

Table 6-3: Techniques which can be employed to open up lithium-ion battery cells once they have been removed from the battery pack structure.

As mentioned, large format pouch and prismatic cells are preferred for this pack configuration due to their ability to stack easily within a module. The cells are stacked and glued together in the stack, with adhesive pads at the stack ends, to ensure rigidity in the module design. Pressure sensitive adhesives are already used in some aspects of battery construction in the form of double-sided sticky pads inside the module case, to maintain an intimate bond between the cell stack and the module case. However, the large contact area makes debonding problematic for disassembly. Removing the cell stack and separating the individual cells from their epoxy resin can take up to 2 hours and require several litres of solvent. This disincentivises careful dismantling and the cells are usually shredded instead. Strategically placed, judicious use of adhesive pads may enable mechanical dismantling and also contribute less mass to the battery module. This could significantly improve the possibility for repair and reuse. While there may be concerns about the structural integrity of EV packs bonded in this way, this sort of approach could be ideal for static battery packs, where mechanical action is less of an issue.

6.2.4 Kyburz case study

EOL battery disassembly has been demonstrated on a commercial scale by the Swiss company Kyburz, who build light weight electric vehicles for private individuals, companies, municipalities, and delivery companies. Their vehicles are powered by lithium iron phosphate cells, and the recycling protocol is claimed to recover > 90% of the battery materials. These materials are then reused in secondary and tertiary applications, such as in 'used vehicles' (~ 85% capacity) and power storage (between 65-85% capacity), respectively.²³ Kyburz uses cylindrical cells in a prismatic conformation, encased in a rigid steel casing. This recycling approach is only viable because no structural adhesives are used between cells, instead the internal components are held together via mechanical fixings, allowing for a simpler, albeit manual and more timeconsuming, module-to-cell separation strategy. This approach is justified, given the relatively small sizes of the battery packs. It does, however, show that disassembly, rather than shredding, can be used if structural adhesive use is minimised. Once the cells are separated, they are opened in an inert atmosphere, using a bandsaw to cut off the terminals and battery management system. The electrode roll is ejected from the casing by drilling a hole in the opposite end of the casing material and applying force using a compressed gas. The polypropylene separator between the electrodes is rewound vertically onto a spindle, allowing the anodes to fall in one direction and the cathodes to fall in the other. These electrodes are immersed in water, allowing a complete delamination. It is thought that a similar methodology can be established when the alternative NaAlg-based electrode binder materials from the previous chapters are used in collaboration with the zigzag conformation and extracellular adhesives discussed above.

6.3 Environmental impacts of utilising alternative design and adhesives

The use of alternative structural adhesives and electrode binders have been identified, both in this work and in previous investigations, to have a significant impact on simplifying battery disassembly.^{15,16} Changes to cell design and the use of novel separation techniques, such as electrode ultrasonication, can form purer waste streams during EOL processing.¹⁴ In this section, the use of alternative adhesives, cell conformations and binders on the global warming potential
and the processing capacity of pack disassembly and electrode delamination are assessed in relation to reference scenarios using commercial pouch cells from a Nissan Leaf. A potential battery dismantling route is shown in **Figure 6-4**. The impact assessments carried out in this work focus on the steps highlighted, as these will be mainly affected by the change in adhesive components. Environmental impact was assessed through global warming potential (GWP), which measures the ability of a greenhouse gas to trap heat within the atmosphere, relative to carbon dioxide, over the course of 100 years.²⁴ This was measured in reference to the IPCC 2013 impact assessment method, with the results given in kg CO₂-equivalents (kg CO₂-eq), which describes the amount of CO₂ that has the equivalent GWP of an emitted amount of greenhouse gas.²⁵ Modelling and calculations were completed using Umberto LCA+ (v. 10.0) software and the Ecoinvent 3.7.1 database was used to acquire necessary data regarding the production and distribution of electricity and any solvent formulation.



Figure 6-4: Flowchart for the battery disassembly route assumed in this environmental impact study. Labels show the steps of the process where the 'Structural Adhesives' and 'Alternative Binders' affect the global warming potential.

6.3.1 Impact of structural adhesives during module opening

Table 6-2 shows that the choice of adhesive will influence the module opening time, which affects both the power requirements for module opening (measured in Wh) and the processing capacity. This study assumes that that the modules are opened with robots as shown in **Figure 6-3**, technical information for the robotics was obtained from their data sheet and is listed in **TableA1**, along with other key parameters used in this assessment.²⁶ The reference scenario considered here is based on data for the Nissan Leaf module-to-cell disassembly previously assessed by Lander *et al.*. This reference scenario permits comparison between the conventional cell design

with structural adhesives, which are assumed to be epoxide based, and the zigzag conformation utilising alternative adhesives.⁴ In the case of the alternative adhesives, the time taken for debonding was estimated based upon the manual debonding times in **Table 6-2**. When robots were used on cells joined with glue dots the time required for debonding reduced by 25%; it was assumed in these scenarios that the automation of disassembly provided a similar reduction in the time taken. **Figure 6-5** shows the GWP, energy usage and process capacity graphs obtained for these module opening scenarios and **Table A2** gives the data behind this figure.



Figure 6-5: Graphs showing the changes in global warming potential (a) and processing capacity (b) values corresponding to the opening of a battery module. The reference scenario assumes the use of a conventional module design and adhesives. The other data assumes the use of the 'zigzag' module conformation with three different adhesive mechanisms.

The first detail that should be noted from this data is the small GWP of this process, regardless of the adhesive used, as it has been shown in g CO₂-eq rather than kg CO₂-eq. In this instance, the low GWP correlates to the relatively low power requirements of the robots in opening the modules and the fact that these values have been determined based on the processing of a single module. The primary difference between the scenarios is the amount of time required to open up the module, which is dependent on the module design. As seen in **Figure 6-5**, a significant reduction in GWP is observed between the reference scenario and the scenarios using the zigzag module design. The time discrepancy between the designs is related to the lack of physical

fastenings like screws, simplifying the process required to dismantle the module and subsequently the amount of operation time the robots need for each module. The choice of adhesive used with the zigzag module is also important for minimising robot processing time and the associated GWP. All of the adhesives tested debond on the timescale of a few seconds. However, debonding of the glue dots was shown to be the quickest and hence shows the smallest GWP, at 250% lower than that of double-sided tape and 125% lower than the Velcro strips.

The reduction in disassembly time will not only affect the environmental impact of battery separation but can also facilitate a higher processing capacity for EOL battery treatments by improving the rate of battery disassembly. Processing capacity was estimated for each scenario based on their respective processing time and the amount of time required for the robot to reset and be ready to open another module, which was found to take around 20 seconds for the robots used in this assessment. Less processing time and a higher throughput of modules, paired with purer waste streams acquired through dismantling batteries over shredding, could have a significant impact on the profitability of recycling facilities, just through simple changes to module design and adhesive materials used in manufacturing.

6.3.2 Impact of alternative binders during ultrasound delamination

The novel ultrasonic delamination technique proposed by Lei *et al.* was selected as the separation method in this study, to assess the effect alternative electrode binders have on battery disassembly. This has already been shown to have a beneficial technoeconomic analysis compared to many hydrometallurgical processes. Only delamination was assessed, so that the environmental impact of replacing the conventional binders can be emphasised. To obtain the input materials for this process from the opened module, the cells acquired in the previous step would have to be opened before the cell components, i.e. electrodes, separators, electrolyte and packaging, are separated into distinct waste streams, ideally via an automated process such as that demonstrated in the Kyburz process.²⁷ Cell opening and separation will also contribute GWP to battery recycling and future work will incorporate these steps into a full LCA study.

Two scenarios were investigated for electrode delamination, one being a reference scenario, using PVDF and CMC/SBR as the cathode and anode binders respectively. This scenario was compared to a hypothetical pouch cell using water miscible binder systems in both electrodes. Data

related to the power, solvent and the time required to delaminate the electrodes was obtained experimentally. **Table A3** shows the parameters assumed for this assessment. Electrode delamination of the cathode and anode will result in the formation of four distinct waste streams; the separated anode/cathode active materials, and their respective current collector foils. The results from this assessment are given with respect to two of these waste streams, the anode and cathode active materials, given in **Figure 6-6**, while all the data acquired, including that related to the current collector foils, is given in **Table A4**.





Figure 6-6a shows a significant reduction in the GWP of ultrasonic delamination when alternative binders are utilised within the electrodes, with the recovery of both types of active material reducing their environmental impact. Figure 6-6b and Figure 6-6c show the power requirements and the GWP associated with solvent usage of ultrasonic delamination. This allows determination of whether the changes to the power output of the ultrasound or the solvents and additives used will reduce GWP the most. Since the anode already uses a water miscible polymer, CMC/SBR, the reduction in GWP is not as extensive as that seen for the cathode, where PVDF is utilised. It is predicted that the only contributing factor to the reduction in GWP of the anode is from no longer requiring the solvent additives. This is because, unlike the binder assumed in the water miscible case, the commercial anode materials require additives, as well as water, to allow for complete and efficient delamination via ultrasound. Table A3 gives the type and amount of additives used for each electrode and the associated environmental impact data was retrieved from the Ecoinvent database. Although the impact that changing the anode material has on GWP is smaller than for the cathode, the elimination of additives and associated manufacturing routes can be significant, when dealing with the considerable amount of battery waste which will be seen in the coming years.

It has been shown in previous studies that while ultrasonic delamination is effective at removing the active material from the current collectors, the binders are still adhered to the active material particles, requiring high temperature processing in order to remove the binder. Anodes using CMC/SBR are also known to undergo extensive cross-linking during manufacturing, causing a significant amount of residue polymer staying adhered to the active material after water-based EOL processing. As stated in chapter 3, the use of NaAlg limits this effect and leads to significantly less binder residue, compared to CMC/SBR, when ultrasound is conducted using water as the solvent. This means that, as well as reducing the energy consumption of the disassembly processes, it also reduces the number of steps required, which would be beneficial to the overall economics and GWP.

Overall, when comparing the reference scenarios to the best alternative scenarios, i.e. using the glue dot and 'water miscible' scenarios, the % reduction in GWP in producing the separate anode and cathode material is 150% and 173%, respectively. It is also thought a similar reduction will be observed in processing costs of battery recycling, when comparing the reference and

alternative scenarios. It is reasonable to assume that novel cell designs, new structural adhesives and water miscible binders will minimise recycling processing costs, with the aim to bring the cost towards the \$45 per pack suggested by Lander *et al.*⁴

6.4 <u>Conclusions and future perspective</u>

This study has shown that while binders and adhesives are one of the most problematic aspects of current recycling processes, as conventional options are manufactured with properties that make subsequent recycling procedures difficult, alternatives can aid in creating recycling process that is economically viable with a minimal environmental impact. Use of larger cells, fewer structural adhesives such as epoxy resins, fully water dispersible electrode binders, reversible physical connectors and alternative cell configurations can all significantly simplify pack disassembly and allow for simple automation procedures. The range of opening techniques discussed in **Table 6-3** show that this approach could be tailored to specific battery chemistries. These design aspects may be easier to apply to batteries used for different applications. For example, static packs used for energy storage experience negligible external mechanical stress so adhesion between packs components may be handled differently from those used in motorsport.

Improved battery design, particularly in vehicles results in easier repair and recycle and can results in improved brand reputation and increased residual values. Design for recycling has the potential to create environmental as well as commercial value. This is seen clearly in section 6.3, where changes to both the adhesives and pack design used were found to have a significant impact on both energy consumption and processing capacity, minimising environmental impact and the cost of disassembly processes. Furthermore, emerging business models such as 'Product as a service', which may aid in advancing circular economies, have the potential to unlock synergistic benefits for producers, if they become responsible for regenerating and recycling products once their initial service life has expired. It can be argued that a clear legal extended producer responsibility that balances the interests of EOL materials recovery with the requirements of second-life,²⁸ coupled with a servitisation model,²⁹ is the best route for promoting many of the goals outlined in this chapter.

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Chapter 7: Conclusions and Future Work

7.1 <u>Conclusions</u>

This investigation has demonstrated how alternative binding materials, throughout the entire lithium-ion battery (LIB) structure can be used to simplify battery disassembly at the end-of-life (EOL). This has primarily focused on alternative water-miscible binders, namely sodium alginate (NaAlg) and gelatin, incorporated into graphite anodes. The delamination efficiency of the anodes was tested using an ultrasonic delamination technique. It was found that complete delamination can be achieved using water as a solvent and lower-powered ultrasound. This was compared to anodes produced using commercial binders such as polyvinylidene fluoride (PVDF) and carboxymethyl cellulose/styrene butadiene rubber (CMC/SBR). NaAlg and gelatin binders reduce the power requirements for the process and eliminate the need for potentially harmful solvents, such as NMP, or solvent additives like citric acid that have been needed for PVDF and CMC/SBR binders. Additionally, it was shown that the active materials obtained from anodes using NaAlg as the binder also contained 76% less binder residues, compared to similar anodes containing CMC/SBR, further highlighting the effectiveness of these alternative adhesives in separating all electrode components and simplifying subsequent recycling steps. Also, environmental impact studies completed in this work details how the global warming potential (GWP) of delamination via ultrasonication can be minimised, by up to 200%, when binders, such as NaAlg are used instead of PVDF and CMC/SBR.

Another key aspect of this work was to show how these water-miscible binders can be altered to improve their performance in battery applications. This was done in several ways, the first detailed in this investigation was modification with a deep eutectic solvent (DES), ChCl:2Gly. Anodes using DES-modified NaAlg and DES-modified gelatin were characterised using TGA, DSC, SEM, AFM, FTIR, contact angle testing, scratch testing and electrochemical cycling. Both of these modified binders resulted in improved adhesive strength compared to PVDF and CMC/SBR. However, FTIR characterisation found that the ChCl:2Gly interacted differently with each polymer. With NaAlg, hydrogen bonding with the glycerol from the DES dominated and replaced associated water with the DES, whilst with gelatin, electrostatic interactions with the DES occurred via the carbonyl groups. This does not replace the associated water, but merely adds DES to the binder system. This had a profound impact on the thermal stability of the electrodes. The removal of moisture increased the thermal stability of NaAlg from $\sim 50^{\circ}$ C to 78°C, eliminating any thermal transitions occurring within standard battery operating temperatures. On the other hand, gelatin showed no thermal stability improvements due to the retained moisture content.

Imaging of the electrodes using various microscopy techniques found that the polymers themselves, while both water miscible, interact with graphite differently. NaAlg interacts with graphite similarly to the commercial PVDF and CMC/SBR binders, whereas gelatin forms an additional polymeric/carbon additive coating upon the electrode surface. Additionally, during electrochemical characterisation it was found that while formation cycles showed minimal differences between the polymers, rate testing revealed that cells using anodes with gelatin binders possessed a lower rate capability (< 0.5C) compared to all the other cells that were investigated. Electrochemical impedance spectroscopy showed an additional impedance contribution that hindered the transfer of lithium ions during cycling. However, anodes using the NaAlg binders showed comparable performance to cells using PVDF, and upon usage of DES-modified NaAlg binders there seemed to be a greater capacity retention at 1C (~ 70 mAh.g⁻¹ higher), which was thought to be related to a better interconnectivity between battery components facilitating easier lithium-ion diffusion, although in-operando studies were deemed necessary to confirm this. From these studies it was clear that, although gelatin presented adhesive and recyclability benefits, the poor thermal and electrochemical stability, even with DES modification, significantly reduces the viability of the polymer as a LIB binder. Meanwhile, NaAlg shows similar adhesive and recyclability benefits and comparable thermal and electrochemical stability and performance to conventional binder materials that are further enhanced through the use of DESs. It is due to this enhanced performance that NaAlg was used in subsequent experiments.

Anodes were remanufactured from reclaimed graphite, from EoL LIBs which was recovered using ultrasonic delamination using NaAlg binders. Unlike the NaAlg cells made with pristine graphite, these cells showed diminished rate performance and increased impedance. This behaviour was thought to correspond to the ultrasound technique itself, causing the fracturing of graphite particles, which during manufacturing of the new electrodes, were agglomerated together. Here, multiple possible adverse processes were identified that could be the source of the capacity fade and impedance rises shown in the electrochemical data. These included electrical isolation of particles due to polymer encapsulation and irregular SEI growth causing localised electrochemistry, such as structural defects and lithium plating. Ultimately, this showed that lower power ultrasound would be beneficial to decrease fragmentation of the anode structure.

Blending NaAlg, and other water miscible polymers, with polyaniline (PANI) was also investigated as a novel binder system using a methodology from literature. Characterisation of both polymer films, created prior to incorporation into electrodes showed that while there was a clear enhancement to conductivity, adhesive strength and thermal stability, PANI modified films did tend to be more brittle. Only the polymer blends with NaAlg and 10 wt% PANI were successful in binding the anodic components together and the anodes produced showed inferior adhesive strength and thermal stability to pure NaAlg binders. Electrochemical testing of the anode created with this binder showed no significant improvement to the capacity of the anodes created, but the voltage profiles and electrochemical impedance spectroscopy data found evidence of side reactions and an improved conductivity for these cells compared to pure NaAlg. Lithiation of PANI to form lithium emeraldinate is thought to shorten the diffusion of lithium ions through the film. In-operando measurements are needed in the future to confirm what the data in this investigation indicates. Overall, the work up until this point has shown that the obvious benefit to recyclability that water-miscible binders, like NaAlg, does not have to mean that the stability or electrochemical performance of the electrodes needs to be sacrificed.

Finally, the design of the packs and the extracellular adhesives used to join cells together were investigated. This study found that changing to an alternative design, such as the zigzag conformation of pouch cells, and using adhesives such as glue dots can drastically reduce the difficulty, time taken (from multiple hours down to ~15 seconds) and environmental impact of pack-to-cell disassembly. This increases the economic viability of battery disassembly over processes such as shredding and simplifies disassembly in such a way that automation of battery dismantling also becomes more viable. Overall, this project has succeeded in showing the importance of alternative adhesives in simplifying battery disassembly and that performance of the battery itself does not have to be lost, and can even be enhanced, if alternative electrode binders, with modifications are utilised.

7.2 <u>Future Work</u>

This project shows some clear routes that need to be explored in improving the performance of alternative binders in LIBs. Techniques, such as Raman could be used to confirm some of the proposed processes occurring during coin cell cycling. It would be useful to understand the interactions between the electrode materials and the binders. Building off of this work would be the investigation into cathodic binders. Initial experiments were made, attempting to use the DES-modified NaAlg to create cathodes. However, extensive cracking was observed which is characteristic of using water-based slurries for cathodes such as NMC. This is due to water leaching lithium from the metal oxide and the subsequent corrosion of the aluminium current collector and gas evolution. While the recyclability benefits for replacing current cathodic binders, with NaAlg-based systems, have been shown in the environmental impact study, a viable system has not been identified yet. It is likely that a successful binder would need to be made from readily available commercial polymers which are blended using an additive package which is amphiphilic. This would enable a water miscible polymer to allow enable dispersion in tan aqueous solvent while an amorphous, probably hydrophobic polymer ensures that the film does not crack and is not brittle. This study has shown that modification or the use of polymer blends can affect key properties of the binder and the electrode itself. Other DESs or polymer blends can be explored in the future to test their viability and continued stability in such cathodic environments. An idealised system would be a binder that can be miscible in non-water slurries, stable in the cathode during use and then be delaminated in water, similar to the anodes shown in this study.

Additionally, as this project focuses on binders for the simplification of battery disassembly before recovery steps, more research into routes of reclamation and remanufacturing of second-life batteries after disassembly should be explored further to optimise the poor performance outlined in part of this work. Such experiments would include examining gentler delamination techniques, rather than ultrasound, for anode materials and the exploration of remanufacturing and cost effective relithiation techniques for cathode materials. Furthermore, there may also be routes to 'recondition' electrodes, restoring electrode performance and chemistry to 'pristine' levels without the need for disassembly, recycling or remanufacturing. It is also necessary to investigate the application of these novel binder systems in next generation battery chemistries, such as lithium-sulfur, sodium-ion and aluminium-based batteries. An assessment of the

applicability of these binders in upcoming battery chemistries would allow confirmation that they can provide continued stability and ensure that the benefits to recyclability are carried through into the future of battery technology. Discussion of these binders, and structural adhesives, would allow for 'design for recycling' to be at the forefront of future battery development and ensure that efficient disassembly and recycling processes can be available from the adoption of these chemistries. Finally, development of a full-scale life cycle assessment (LCA) detailing the environmental and economic impact of the manufacturing and recycling of electrodes and packs, using the types of adhesives investigated in this thesis is essential in determining the true viability of these novel adhesives in future battery technologies.

Appendix

This section contains figures and tables that are supplementary to the main text, such as additional electrochemistry data from chapter 4 and the data inputs for the environmental impact study in chapter 6. Also shown here are copies of the papers written using work present in this thesis.



Figure A1: Voltage profiles for the remaining DES-modified binder systems not observed in Figure 4-2. a) gelatin 100, b) gelatin 80, c) NaAlg 100, d) NaAlg 80



Figure A2: Waterfall plots for the remaining DES-modified binder systems not observed in Figure 4-3. a) gelatin 100, b) gelatin 80, c) NaAlg 100, d) NaAlg 80

Table A1: Key parameters used in the calculation of the data related to the module to cell
disassembly for the Nissan Leaf reference scenario and the zigzag module design experiments.
Results are shown in Figure 6-5 and Table A2.

Module Opening Parameter	Reference Scenario	Glue Dot	Velcro Strip	Double Sided Tape
Module Design	Conventional Nissan Leaf Module		Zigzag Conformatio	n
Robot Power Consumption	80 W for contr	ol unit, 300 W for	robot arm (85-90%	of max power)
Dismantling Time Per Module*	738 s (0.205 hr)	15 s (0.0042 hr)	19 s (0.0053 hr)	38 s (0.0105 hr)
Robot Reset Time		2	0 s	
Electricity Grid Mix	Average grid mix from 2021 with production data obtained from Ecoinvent 3.7.1 Database Grid Mix - 35.7% Gas, 16.1% Nuclear, 13.0% Offshore wind, 12.6% Biogas, 11.1% Onshore wind, 4.2% Solar, 2.6% Biomass, 2.0% Hydroelectric, 1.8% Coal, 0.5% Pumped Storage and 0.4% Oil			

* Times were 75% of the times quoted for manual disassembly from this study and the previous study by Lander et al. for the reference scenario to account for automation.

Table A2: Global warming potential, energy usage and process capacity values corresponding to Figure 6-5. The reference scenario assumes the use of a conventional Nissan Leaf module design and structural adhesive using data from Lander et al. The other data assumes use of the zigzag module design for each of the quoted adhesives.

Module Design	Pressure Sensitive Adhesive	GWP (g CO2 equiv.)	Energy Usage (Wh)	Process Capacity (Modules per hour)
Conventional Design (Nissan Leaf 2018 Tekna)	Conventional Adhesive (thermoset polymer)	20.1	77.9	3
Zigzag Conformation	Glue Dot	0.402	1.52	100
	Velcro Strip	0.502	1.90	90
	Double Sided Tape	1.00	3.80	75

Table A3: Key parameters used in the calculation of the data related to the delamination of the electrodes using ultrasound. The reference scenario corresponds to an electrode using conventional binders and the water miscible scenario relates to electrodes using alternative, alginate binders in both electrodes.

Ultrasound Delamination Parameter	Reference Scenario	Water Miscible Scenario	
Number of Electrodes	22 Anodes, 21 Cathodes		
Binders	Anodes – CMC/SBR Cathodes – PVDF	Both – Sodium Alginate	
Ultrasound Power Consumption	4.0 kWh at 100% Power Output		
Ultrasound % Power Output	Anodes – 10% Cathodes – 100%	Both - 10%	
Solvent Additives Needed	Anode - 0.1M Citric Acid Cathode - 0.2M NaOH	N/A	
Amount of Solvent (L)	2.5 (Delamination), 2 (Filtering)		
Total Delamination Time	516 s (0.14 hr) [12 seconds for one electrode, 43 electrodes total]		
Sheet Feeder Power Consumption	0.20	kWh	
Drying Oven Power Consumption	0.75	kWh	
Drying Time	Anodes – 3 hr Cathodes – 12 hr	Both – 3hr	
Electricity Grid Mix	Average grid mix from 2021 with pro 3.7.1 D Grid Mix - 35.7% Gas, 16.1% Nuc Biogas, 11.1% Onshore wind, 4 Hydroelectric, 1.8% Coal, 0.5%	duction data obtained from Ecoinvent atabase clear, 13.0% Offshore wind, 12.6% .2% Solar, 2.6% Biomass, 2.0% 6 Pumped Storage and 0.4% Oil	

Product from Separation	Reference Scenario	Water Miscible Scenario	
	Total Global Warming Potential (kg CO ₂ equiv.)		
Anode Active Material	1.74	0.87	
Cathode Active Material	3.46	0.89	
Aluminium Foil	0.02	0.003	
Copper Foil	0.05	0.004	
	Delamination Energy Usage (kWh)		
Anode Active Material	3.09	3.09	
Cathode Active Material	10.34	3.09	
Aluminium Foil	0.59	0.09	
Copper Foil	0.09	0.09	
	Global Warming Potential Rela (kg C	ating to Solvents and Additives Used CO ₂ equiv.)	
Anode Active Material	0.85	0.06	
Cathode Active Material	0.65	0.07	
Aluminium Foil	0.02	0.002	
Copper Foil	0.04	0.003	

Table A4: Global warming potential, power consumption and associated solvent GWP values corresponding to Figure 6-6. The reference scenario assumes the use of conventional binders within the electrodes (PVDF - cathode and CMC/SBR - anode) and the water miscible scenario assumes alginate binders for both electrodes.



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Gelatin and Alginate Binders for Simplified Battery Recycling

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ABSTRACT: The water-soluble biopolymers, gelatin and sodium alginate, were investigated as potential alternative binders for use in lithium-ion battery anodes. The polymers were modified using a deep eutectic solvent (DES) made from choline chloride and glycerol. It was found that the addition of the DES resulted in greater plasticity and adhesion with respect to the unmodified binders and also to the current commonly used PVDF or CMC/SBR binders. Both the modified gelatin and sodium alginate binders are dispersible in water and can be rapidly delaminated by using mild ultrasound. These latter points are key steps in the function of the anode material and the subsequent recycling at the end of life. Imaging of the coatings formed using scanning electron microscopy and atomic force microscopy showed that the two types of binders dispersed themselves differently around the graphite particles, with the gelatin binder being distributed across the entire electrode



surface, whereas the sodium alginate binder remained located at the hydrophilic edge planes of the graphite.

1. INTRODUCTION

Lithium ion batteries (LIBs) are the intermediate solution to reduce the emission of greenhouse gases in the transportation sector through electric vehicles (EVs).^{1,2} The EV global market share is growing rapidly and 2020 saw 3 million EV registrations to produce a global stock of 10 million vehicles.³ This increased adoption will naturally produce a waste stream that will need to be processed. Harper *et al.* predicted that from the 1 million vehicles sold in 2017 alone, 250,000 tonnes of battery waste would be produced once they have reached the end of life (EOL).⁴ While a portion of this waste may be treated *via* the current recycling processes to recover the critical materials for reuse, it is likely that these processes will become overburdened in the near future, given the current trajectory of EV sales.

The current design of LIBs makes recycling complex and inefficient compared to lead acid batteries and considerable effort is now being invested in the concept of design for recycle.^{4,5} Recovery of the electrode-active materials, such as cobalt, lithium, and graphite, is especially important as these are all present on US and EU critical material watch lists.^{6,7} The economics of the recycling process are controlled by the purity of the products, and techniques, which shred cells, are compromised by the low purity "black mass" produced. A recent techno-economic comparison by Thompson *et al.* indicated that physical separation of the battery components prior to delamination is more profitable than shredding due to the formation of purer waste streams.⁵ Lei *et al.* proposed a method to separate the active material from the metal foil

using high powered ultrasound.⁸ The method breaks the adhesive bond, delaminating an electrode in just a few seconds. However, the process was highly dependent on the binder type present within the electrode. Water-dispersible binders would simplify this process, and the present study investigates two such binders.

The most common binder used in both LIB cathodes and anodes is polyvinylidene fluoride (PVDF) chosen for its inherent electrochemical stability resulting from its oxidative resistance. It also contributes to a surface passivation layer on the anode that hinders reductive decomposition of the electrolyte and extends battery life.^{9,10} However, the use of PVDF binders exhibits significant limitations when it comes to recycling processes, as PVDF is poorly soluble except in *N*methyl-2-pyrrolidone (NMP), which is an expensive and toxic solvent. The chemical stability of PVDF means that high temperature processes are required to decompose the polymer and recover the active material and these result in byproducts including HF and CO, which must be scrubbed from flue gasses.⁴

Recently, alternative binders, such as carboxymethyl cellulose (CMC)/styrene butadiene (SBR) and CMC/polyur-

Received:February 22, 2022Revised:April 19, 2022Published:May 5, 2022







Figure 1. Molecular structures of the gelatin (a) and sodium alginate (b) and the DES components choline chloride (c) and glycerol (d) used in this study.

ethane (PU), have become more common because CMC is water-dispersible.^{11,12} Other water-dispersible binders, which could enable facile separation of the active material from the current collector, include the use of guar gum,^{13,14} acrylates,^{14,15} gelatin,^{14,16} sodium alginate,^{14,17,18} and chito-san^{14,19} Use of these can result in the production of higher purity waste streams, which will simplify subsequent recycling processes.

Gelatin is one of the most versatile naturally occurring biopolymers and has been used in several gel-based bioadhesives.²⁰ This has led to investigations into its use in electrode binders.^{21,22} Gelatin is a heterogeneous mixture of single or multistranded polypeptides made up of glycine and proline residues, containing both hydrophilic and hydrophobic groups (Figure 1a). This amphiphilicity allows for emulsification into water, while being insoluble in organic solvents. Similarly, alginate-based polymers have also been investigated as bioadhesives and binder materials previously, often having to be modified to reduce the brittleness of the polymer.² NaAlg can be sourced from brown seaweed, and like gelatin, it is cheaper than PVDF. It is composed of 1,4-linked β -Dmannurate and α -L-guluronate moieties and possesses a polymer structure capable of extensive hydrogen bonding (Figure 1b). NaAlg was first studied as a potential binder for Si-based anodes by Kovalenko *et al.*,²⁴ and subsequent studies have demonstrated the effectiveness of NaAlg as a binder for cathode materials such as NMC111 (LiNi_{0.33}Co_{0.33}Mn_{0.33}O₂) and LNMO (LiNi_{0.5}Mn_{1.5}O₄).^{25,26}

In their pure forms, both gelatin and NaAlg are relatively brittle but a recent work has shown that several biopolymers can be plasticized using deep eutectic solvents (DESs),^{27–32} which are eutectic mixtures of a quaternary ammonium salt and a hydrogen bond donor.³³

The main aims of this study were to characterize and compare anode electrode samples created using gelatin and NaAlg (both modified and unmodified) with a PVDF binder. The mechanical and thermal properties of these electrodes were investigated before testing delamination using the ultrasound processing methodology outlined by Lei *et al.*⁸

2. EXPERIMENTAL SECTION

The chosen DES (ChCl:2Gly) was formed by heating and stirring a 1:2 molar ratio of choline chloride (ChCl) (SLS,

100%) and glycerol (Gly) (Fisher Scientific UK, laboratory grade) at 60 $^{\circ}$ C until a homogeneous colorless liquid is formed.^{34,35} Before use, the DES was stored in a sealed container at room temperature to prevent moisture absorption and any heat-related decomposition of the DES components that may occur.

The coated electrodes used in this study were manufactured via a conventional slurry-based methodology. The two polymers were gelatin (Sigma-Aldrich, 100%) and sodium alginate (ACROS Organic, 98%). These were initially combined with the DES in the presence of 5 mL of deionized water to form the binder solution. The binder solutions had varying ratios of polymer-to-DES (100:0, 90:10, and 80:20) but always made up 10 wt % of the overall mass of the electrode slurry that was produced. Carbon black super P conductive additive (Alfa Aesar, >99%) and C-NERGY spherical graphite (Imerys graphite and carbon, >99%, ≈ 15 μ m particle size) were then added in increments, along with an additional amount of deionized water (3 mL for gelatin and 7 mL for NaAlg) in order to form a thick, homogeneous slurry, before being stirred in a SciQuip Vortex Varimax mixer. The slurry was then applied to a 25 μ m thick copper sheet via the use of a Sheen Automatic Film Applicator equipped with a square doctor blade set at a 200 μ m thickness, at a rate of 50 mm s⁻¹. Once cast, the electrodes were left to dry at 40 °C in a fanless Genlab Classic Oven (MINO/50) before being calendered using an MSK-HRP 1A rolling press (MTI Corporation) set at 40 °C at a rolling speed of 6 mm/s. PVDF (Alfa Aesar, 100%) and CMC/SBR (BDH Chemicals, >99%) electrodes were also created using the same methodology, although the creation of the PVDF slurry used Nmethyl-2-pyrrolidone (BDH Chemicals, >99%) as the solvent rather than deionized water. The binder content for the reference electrodes was 10 wt %, and so, a direct comparison can be made between these reference materials and the modified gelatin and sodium alginate electrodes with regards to their mechanical and physical properties.

Scanning electron microscopy (SEM) was carried out using a FEI Quanta 650 FEG-SEM in secondary electron mode, with an Everhart Thornley detector. Atomic force microscopy (AFM) was carried out using a Bruker Dimension Icon AFM with a Nanoscope V controller and Nanoscope 9.4 imaging software. AFM was carried out using the peak force tapping

(PFT) imaging mode. This involves oscillating the cantilever by placing the probe upon the surface at a frequency below that of the resonance frequency. In this mode, the probe comes into contact with the surface until a specified force set point is reached, generating a force versus time curve for every pixel of the image allowing modulus values to be generated from these curves. This allows for the identification of the different electrode components on the surface, as done previously for NMC by Terreblanche et al.³⁶ A RTSEP-300 probe with a spring constant of 40 N/m was used to acquire the height images and data used by the Nanoscope 16.4 software to calculate the Sneddon Modulus, giving a modulus scan of the surface. Scratch testing was carried out using a ST200 scratch tester with a diamond probe. The scratches were analyzed with a Zeta-20 3D optical profiler. Three scratches were made on each sample in order to get an average scratch length to determine the standard deviation.

Two techniques were used to acquire the thermal characterization data for this study. Differential scanning calorimetry (DSC) was carried out across a heating range of 25-500 °C, with a heating rate of 5 K min⁻¹, using a Mettler Toledo DSC1, with samples placed within 100 μ L aluminum pans during analysis. Due to the high heat capacity of the graphite and copper, polymer transitions could not be seen when analyzing the whole electrodes, and so, the binder solutions on their own were measured to show how the modification of the polymers by the DES affects their thermal stability. Reference samples of the unmodified polymers and the DES were measured to aid in identifying transitions. Thermogravimetric analysis (TGA) was also completed using a Mettler Toledo TGA/DSC1 using the same sample pans, heating range, and heating rate. The data from these experiments are not discussed in this paper, but the full thermal characterization from the DSC and TGA data is given in the Supporting Information.

Wettability testing was carried out on electrode samples cut into samples 1 cm² in area and stuck onto a glass slide using double-sided tape to ensure the material was as flat as possible. Analysis was carried out with a Biolin Scientific Theta Lite One Attension optical tensiometer, underneath a syringe filled with deionized water that was equipped with a square-cut needle. One Attension software (version 2.5) was used to obtain the contact angle over a period of 20 s, with the last recorded value over this period being used to give the value quoted within this work.

Delamination of the graphite-binder coatings from the copper foils was carried out using ultrasonic techniques at two different power intensities, with water as the solvent. For the low power method, an ultrasonic bath was used (power intensity ≈ 0.02 W cm⁻²). The electrodes were cut to 3 cm² and placed within a beaker filled with 75 mL of deionized water. The beaker was placed within a Fisherbrand FB15055 ultrasonic bath for 5 min at room temperature. For the high power method, a commercial ultrasonic system (Branson Sonics, 1.25DCXa20-V) was used. This system has a cylinder sonotrode of 20 mm diameter, operating at 20 kHz, with a power variable of up to 1250 W, which can deliver a power intensity of up to 398 W cm⁻². The electrodes were cut into an area of 3 cm² and stuck down onto a custom-made plastic platform, which itself was stuck down onto the bottom of a beaker. This was done to ensure that the sample was secure and level during the experiment, ensuring uniform interaction between the ultrasound waves and the electrode surface. The

beaker was then filled with 75 mL of deionized water, and the sonotrode was lowered into water and turned on at 10% power for 5 s. After ultrasonication, all samples were washed with deionized water and dried in the fanless oven used previously at 30 °C before any further analysis was carried out.

3. RESULTS AND DISCUSSION

Anode electrode samples were fabricated from a mixture of the active carbon components, polymer, and DES, using a slurry and doctor blade methodology described in the experimental section. A range of coated electrodes were prepared, so as to compare the morphology and the physical and mechanical performance of the gelatin and alginate binders using different ratios of polymer to DES plasticizer with those of materials created using conventional PVDF and CMC/SBR binders.

3.1. Coating Morphology. The electrode morphology was examined using SEM to determine the location of the binder and carbon black (CB) around the larger graphite particles. It was observed that the morphology of both the gelatin and sodium alginate electrodes is typical of a graphite anode material made with PVDF; however, the gelatin samples exhibit pin-hole defects (Figure 2). When formed, these pin



Figure 2. SEM image showing examples of the pin-hole defect present upon the modified gelatin electrode surfaces. The image was acquired using an excitation voltage of 10 kV.

holes can propagate *via* a self-catalytic process, whereby the thermodynamics and kinetics of surface electrochemistry are promoted where the pin-hole defects are located. This localization and accumulation of surface chemistry at these heterogeneities will lead to additional deformities, further catalyzing additional localized reactions and resulting in premature electrode failure.³⁷ The hygroscopic nature of the gelatin³⁸ and the ChCl:2Gly, coupled with the water-based slurry used to create the electrodes, is the source of the pin-hole defects as a relatively large degree of associated water content is present within the initial cast. Upon drying, the expelled water leaves the pits behind.

Figure 3 shows SEM images of the graphite-active material for both the modified gelatin and sodium alginate electrodes (images a and b) *versus* the reference electrodes made with PVDF and CMC/SBR (images c and d, respectively). In the gelatin image, the graphite particles are covered in smaller particles, presumably the CB. The coverage of these particles across the entirety of the graphite, rather than being situated between the particles, is unlike that seen in conventional PVDF and CMC/SBR electrodes, as well as the behavior observed in the NaAlg image. Typically, a LIB binder will separate into



Figure 3. SEM images showing surface morphology of graphite bound with (a) gelatin and (b) sodium alginate both modified 10 wt % [ChCl:2Gly] (c) PVDF and (d) CMC/SBR. All images were taken using an excitation voltage of 10 kV.

three states during interaction with a surface-bound polymer, where the polymer chemically bonds or adsorbs to the particle surface at bonding sites, an immobilized polymer, where the polymer layers of neighboring particles interact, and a free polymer, where the polymer is distributed across the active material particles.³⁹ PVDF binds to oxygenated hydroxyl and carbonyl groups located on the edge planes of the graphite due to its polarity, with immobilized layers existing in the interstitial sites between graphite particles and free polymers being rarely distributed across the electrode surface.⁴⁰ For gelatin, the polymeric region seems to exist across the entire surface rather than being localized to the edge planes and gaps between the graphite. As gelatin is an amphiphilic polymer, capable of interactions with hydrophilic and hydrophobic materials, it could be interacting with the main body of the graphite, as well as the edge plane, thereby expanding the bound and immobilized polymer layers to the entire electrode surface. On the other hand, the NaAlg electrodes seem to behave similarly to the reference electrodes, with polymeric regions mainly existing toward the edge planes of the graphite and the areas between the graphite particles. As NaAlg is hydrophilic, rather than amphiphilic, it will not bind to the bulk of the graphite particles, instead it localizes to the edge planes where it is possible to undergo hydrogen bonding with the hydroxyl and carbonyl groups. From there, the immobilized phase will form with neighboring polymeric regions with sporadic distribution of the free polymer on the graphite surfaces.

In order to confirm the observations made in these SEM images, modulus scans using AFM were recorded (Figure 4). AFM data were acquired in peak-force mode. Here, the AFM scan produces modulus data through the probe coming into contact with the surface until a set point is reached, generating a force—time curve for every pixel on the image. Terreblanche *et al.* used this technique to identify the different electrode components for NMC cathodes, and the same technique and modulus models were used in this study.³⁶ It should be noted that the modulus images show a semiquantitative, comparative

contrast in the modulus values; quantitative values for the modulus could not be acquired for these samples. The sample modulus is calculated using tip dimensions, such as the tip radius and tip angle. When the AFM tip is incident on a sample surface, these dimensions can change due to deformities and wear. This will therefore affect the calculated modulus values, meaning that these values can no longer be taken as "absolute" values. For the present application, a self-consistent comparative analysis is sufficient to make a distinction between the "hard" graphite and the "soft" polymer and CB. Overall, the AFM images support the observations made from the SEM images, reinforcing the proposed differences in how each polymer binds to the graphite-active material. The darker areas of the images on the right-hand side correspond to the softer regions of the sample, that is, the polymer and CB. The lighter areas correspond to the harder regions, that is, the graphite.

In the case of the gelatin sample (Figure 4a,b), the entire sample surface is covered in these darker regions, confirming the presence of a polymer/CB layer. The morphological image in Figure 4a shows sub- μ m particles in the same area as the "dark" overlay in the modulus scan, confirming the presence of the CB in these polymeric regions. The presence of this polymer/CB layer across the entire electrode surface could influence both the mechanical and electrochemical behavior of these electrodes. First, it could strengthen the adhesive bonding, as extra mechanical force may be required to penetrate the surface layer before adhesive bonds between the graphite particles and the copper foil are broken. Second, this layer may affect the performance of the battery, as intercalation of the Li ion may be hindered, or result in changes to the formation of the solid electrolyte interface that is essential for stabilizing the anode during cycling.

The NaAlg images (Figure 4c,d) show a more typical electrode format, where the "softer" polymeric regions exist on the edges and in between active material particles. The pronounced edges between the two regions showcase the inability of NaAlg to interact with the majority of the graphite particles due to their hydrophobic nature. The lack of resolved

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Figure 4. AFM images for graphite electrodes showing the surface morphology and modulus scans for electrodes used in this study, taken over a 5 \times 5 μ m area. The polymers used as the binders included (a,b) gelatin:(ChCl:2Gly), (c,d) sodium alginate:(ChCl:2Gly), (e,f) PVDF, and (g,h) CMC/SBR.

CB particles in the morphological image also indicates a weaker interaction between the polymer and the CB compared to gelatin. The reduced interaction with the hydrophobic components may indicate a reduced mechanical strength compared to that of gelatin, with less adhesive interactions that need to be broken and the lack of this layer of polymer and CB on the electrode surface. The AFM images of the PVDF and CMC/SBR reference electrodes (Figure 4e-h) show behavior

similar to those of NaAlg, reinforcing what was seen with the SEM images and emphasizing the morphological difference between the hydrophilic (NaAlg and CMC/SBR) and polar materials (PVDF) *versus* the amphiphilic gelatin as a result of gelatin being able to interact with all electrode components.

SEM and AFM have allowed for the determination of the polymer location within the electrode systems and have clearly shown the key differences between both polymers based on

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their natures. Potential issues surrounding the electrochemical and mechanical stabilities of these electrodes have also been outlined based upon the location of the polymers and defects found on the electrode surface. Mechanical characteristics of the electrodes as a result of polymer interactions with the active material and surface defects will be discussed in subsequent sections, and further studies into electrochemical properties will be conducted at a later date.

3.2. Adhesion Testing. Gelatin and NaAlg are both known to be brittle materials, withstanding high loads, but breaking apart without much elongation when sufficient force is exerted. Modification with DESs such as ChCl:2Gly has been effective in improving the degree of elongation in gelatin previously,²⁷ and similar modifications have previously been effective at reducing brittleness in NaAlg²³ through plasticization of the polymer chains. A similar effect is in effect here, with the added flexibility of the polymers increasing the total adhesion strength of the materials upon addition of 10 wt % ChCl:2Gly to the binder systems.

The adhesion strength of the electrode to the current collector was determined by the scratch test method. In this case, this involved creating a scratch on the electrode surface with a set starting and ending load. By obtaining the distance from the start point of the scratch to the point where the copper current collector can be observed, the critical load (Lc) applied at this distance can then be calculated using the set load rate (40 N/min) and table speed (200 mm/min). The Lc is a measure of the adhesive bond strength between the active material binder and the current collector, and higher magnitudes of Lc correspond to a better adhered, more mechanically stable electrode. Table 1 shows how the adhesive

 Table 1. Scratch Test Data Showing the Critical Load

 Distribution With Changing Binder-to-ChCl:2Gly Content

 for Gelatin and Sodium Alginate Samples^a

polymer	critical load (N)
PVDF	3.59
CMC/SBR	3.29
gelatin-no ChCl:2Gly	6.39
gelatin-10 wt % ChCl:2Gly	6.53
gelatin-20 wt % ChCl:2Gly	6.24
NaAlg-no ChCl:2Gly	4.19
NaAlg-10 wt % ChCl:2Gly	5.68
NaAlg-10 wt % ChCl:2Gly	2.89
^a DES-free PVDF and CMC/SBR are incl	luded as reference points

strength of the electrodes created with gelatin and NaAlg changes with ChCl:2Gly content. The most notable aspect is the superior Lc of both gelatin and NaAlg compared to the conventional anode binder materials, PVDF and CMC/SBR. The high adhesive strength of these polymers *versus* the conventional materials exhibits how electrode performance, as well as end-of-life treatments, could be improved by changing the binders.

Modification of NaAlg has a greater effect on Lc compared to that of gelatin, which suggests that the DES interactions are more extensive with NaAlg. This could be related to the relative size of the molecules and the steric factors that may limit the available sites for polymer–DES interactions to take place, limiting the degree of plasticization that may occur and subsequently the deviation in flexibility and Lc. However, even with the improvements the ChCl:2Gly makes to the adhesion strength of NaAlg, it still possesses a strength lower than that of all the gelatin electrodes investigated here. This may be related to the even coating of the material across the gelatin electrode surface, which may increase the external forces required to overcome the adhesive intergraphite and graphitecurrent collector bonding as this layer needs to be penetrated first. Alternatively, the reduced adhesion strength could be a function of the reduced amount of interactions NaAlg will have with the hydrophobic graphite compared to gelatin, thereby reducing the number of adhesive forces and keeping the electrodes together.

3.3. Thermal Characterization. Thermal characterization of the binder materials was carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), with comparison being made to the key thermal transitions of conventional PVDF and CMC/SBR electrodes. The binder solutions containing gelatin and NaAlg at each of the ChCl:2Gly compositions were investigated using DSC to observe any changes to the thermal stability of the materials as a function of the changing ChCl:2Gly content (Figure 5). This



Figure 5. DSC curves showing change in heat flow as a result of the dehydration and melting transitions of the DES-modified polymer binders investigated in this study. PVDF and CMC/SBR materials were used as a reference to conventional materials.

was to avoid deviations in the onset temperatures and enthalpy values that would result from the high heat capacity of copper and graphite. The full thermal characterization data for each polymer/DES composition, including the onset temperatures, enthalpy changes, derived from DSC, and mass losses derived from TGA analysis for each observed transition, are given in Table S1.

The thermal stability of gelatin is the lowest of the polymers investigated in this study, with the earliest transition occurring at around 40 °C, relating to a trans-conformation transition, where the gelatin changes from a helical to a coiled configuration.⁴¹ This transition occurs within the standard battery operating temperature range (from -20 to $60 \degree C$) and could lead to significant issues with electrode fracturing and unwanted side reactions. The close proximity of this initial transition to the glass transition temperature and the melting point of gelatin causes the broad peak observed in Figure 5. Addition of ChCl:2Gly does not improve the thermal stability, with the onset temperature of this transition decreasing as ChCl:2Gly is added. When investigating the thermal properties of gelatin, Michon et al. proposed that association of helical gelatin structures via hydrogen bonding was localized to "junction zones", which were the first features to be lost upon heating.⁴¹ The presence of ChCl:2Gly could limit the

formation of these zones, with the additional choline chloride and glycerol molecules hydrogen bonding with the functional groups of the gelatin, acting as a buffer between neighboring chains, and reducing polymer—polymer interactions and the formation of these "junction zones".

NaAlg has a broad initial transition similar to gelatin, which has been attributed to the dehydration and melting of the polymer. However, upon modification with ChCl:2Gly, this transition shifts to higher onset temperatures, increasing from 50.85 °C when unmodified, to 78.45 °C in the "80:20" sample. This is of comparable thermal stability to CMC/SBR, which undergoes a melting transition onset at 84.21 °C. The reason behind the shift has been attributed to the water that is typically hydrogen bonded to the -COO⁻ group of NaAlg,⁴² being replaced by glycerol from ChCl:2Gly due to the similar bonding capabilities between glycerol and water. The fact that this peak is shifting, rather than just becoming even broader, indicates the replacement of water by glycerol rather than them both being present. This is of particular significance due to the fact that through the modification of NaAlg, the thermal stability of the polymer is now outside the LIB operating temperature range and comparable to a polymer that is already used in LIB anodes. This greatly reduces the risk of electrode degradation and unwanted side reactions that could occur with thermal events occurring within this range.

3.4. Wettability Testing. The wettability of these electrode materials by water was characterized by measuring the contact angle of water when incident on the sample surfaces. Figure 6 shows a schematic diagram of the



Figure 6. Schematic diagram showing the difference between the internal and external contact angles.

measurement of the contact angle, which can be done in two ways giving an internal or external contact angle. This study will use the internal contact angle from this point on, with the data acquired for each sample being shown in Table 2.

Table 2. Contact Angle Values for the Modified Gelatin and Sodium Alginate Electrodes *vs* the Unmodified Materials and a PVDF Electrode as a Reference When Water is Used as the Solvent

polymer	contact angle (°)
PVDF	119.68
gelatin-no ChCl:2Gly	92.02
gelatin-10 wt % ChCl:2Gly	95.50
gelatin-20 wt % ChCl:2Gly	110.29
NaAlg-no ChCl:2Gly	68.30
NaAlg-10 wt % ChCl:2Gly	67.11
NaAlg-10 wt % ChCl:2Gly	65.88

Wettability indicates how well water permeates into the electrode material, and whether gelatin and NaAlg still show hydrophilicity after incorporation into these electrodes. Materials showing contact angles of less than 90° are considered "wetted" by water, whereas those with contact angles greater than 90° are considered "nonwetted" samples. A reference electrode containing the PVDF binder provided a contact angle value of 119.68° , that is, "nonwetted", which is expected from the hydrophobic nature of both PVDF and graphite.⁴³

All of the electrodes containing the gelatin binder show contact angles of greater than 90° due to the amphiphilic nature of the polymer paired with the hydrophobic nature of the graphite. As the ChCl:2Gly content increases, so does the contact angle value, potentially due to a decrease in the number of available hydrophilic interaction sites caused by the interaction of gelatin with glycerol. Some limited permeation of water into the electrode is likely, but it is unlikely to be uniform.

The binder systems containing NaAlg all have contact angle values of less than 90° , indicating successful surface wetting with water. In these systems, the addition of ChCl:2Gly instead resulted in a slight decrease in the contact angle. While thermal data showed that the addition of DES caused replacement of associated water content with glycerol molecules, there may still be available interaction sites for water to bind to, providing a route water can take through the material. Overall, the wettability data indicate that NaAlg interacts with and takes on water relatively easily, but the gelatin materials do not, which may lead to issues with potential recycling procedures for gelatin electrodes.

3.5. Recyclability Studies Using Ultrasound. Ultrasound techniques were employed to show the efficiency of electrode delamination when these novel binders are utilized. The electrodes were submerged in deionized water to observe whether the use of water-soluble binders does facilitate recycling processes and limit the need for harsher, more expensive solvents or additives, which are required for some commercial materials.⁸ Due to the water-soluble nature of these polymers and the effectiveness of this method on CMC/ SBR electrodes reported previously,⁸ a low-powered ultrasonic bath system was tested first to show how further improvements to the ultrasound separation could be made by using these binders. Figure 7 shows the electrodes before and after processing in the ultrasonic bath to show the degree of delamination the procedure incurs. Even though both polymers are water-soluble, they behave differently, with NaAlg almost fully delaminating within the first 30 s of sonication. It is predicted that water is sufficient to break the majority of the adhesive bonds, with the ultrasound acting as a catalyst to improve the rate of separation. On the other hand, the gelatin electrodes retain the majority of the active material after processing with the ultrasonic bath. The amphiphilic nature of gelatin means that water will already be associated in the polymer system, limiting the ability to associate with bulk water to disrupt adhesive bonding. Some defects such as cracking and pin-hole defects are formed during the ultrasonication process (Figure 7b), which shows that ultrasound affects the cohesiveness of the active material. Full delamination may be possible through the use of a high-powered ultrasonic horn, similar to that used by Lei et al.⁸

Figure 7e,f shows the images for the gelatin electrode before and after high intensity ultrasound processing. A power output



Figure 7. Images showing electrodes before and after processing with different ultrasonication techniques. An ultrasonic bath (power intensity $\approx 0.02 \text{ W cm}^{-2}$) at room temperature for 5 min is used in images (a–d). (a,b) Gelatin electrode and (c,d) sodium alginate electrode. (e,f) Effect of a high-powered ultrasonic horn (power intensity $\approx 398 \text{ W cm}^{-2}$) on the gelatin electrodes at 10% power for 5 s.

of only 10% for 5 s was sufficient to delaminate the active material from directly underneath the sonotrode, as well as inducing more extensive cracking of the electrode in the surrounding area. It is thought that by utilizing a continuous flow process, full delamination of the gelatin electrodes can be achieved using high-powered ultrasound on a 10% power setting, without the use of expensive solvents or additives, as water is sufficient to delaminate these materials.

3.6. Electrochemistry—Proof of Concept. As stated previously, full electrochemical characterization of the graphite electrodes created using these gelatin- and alginate-based binders will be presented in a separate article. However, the importance of electrochemical analysis when discussing new electrode materials is imperative. Included below, in Figure 8, is the discharge/charge voltage profiles and associated plot showing how the discharge capacity, charge capacity, and Coulombic efficiency change across the initial cycling for a NaAlg 90 electrode in a coin half-cell using Li-metal as the counter electrode and Li⁺ source. These initial cycles were completed at 0.1 C between 1.5 and 0.065 V (vs Li⁺/Li), with these parameters being utilized to promote SEI growth and sufficient lithiation of the graphite. After these cycles, the discharge capacity was 214 mA h.g⁻¹ with a charging capacity of 190 mA h.g⁻¹ and a Coulombic efficiency of around 89%. While this efficiency is still relatively low, compared to what would be expected out of lithium-ion batteries (typically >95%), it is something that can be optimized when analyzing the full electrochemical characteristics of these materials in the future.

4. CONCLUSIONS

DES-modified gelatin and NaAlg-based binders were successfully used to make electrode coatings on copper foil substrates. The morphology of these electrode coatings was characterized using SEM and AFM, and it was found that the gelatin binder formed a polymeric layer across the surface of the electrode, whereas the NaAlg binder behaved in a manner similar to PVDF, in that it was located in discrete locations around the edges of the graphite particles. The plasticizing effect of ChCl:2Gly on gelatin and NaAlg resulted in a higher adhesive strength of the material versus electrodes made with the industrially used binders PVDF and CMC/SBR. However, only the modified NaAlg system showed thermal stability comparable to a CMC/SBR system, as thermal degradation of gelatin took place within the normal operating range of a lithium-ion battery. The physical and mechanical properties of these binders outside of a working battery system show promise for application in lithium-ion batteries; however, further work must be carried out to ensure that they do not impact adversely on cycling behavior.

The recyclability of these films was tested by observing the degree of delamination of the gelatin and NaAlg coatings, first in an ultrasonic water bath and, in the case of gelatin, using high-powered ultrasound (10% power). Both samples showed improved recyclability compared to PVDF samples, exhibiting



Figure 8. Preliminary electrochemical characterization for a NaAlg 90 sample in a Li-metal half-cell (0.1 C, 1.5-0.065 V vs Li⁺/Li). (a) Initial discharge/charge voltage profile and (b) discharge (black) and charge (red) capacity for each cycle with the associated charging efficiency (blue).

how changing the binder within LIBs can have a profound effect on the separation of the active material and current collector, reducing energy requirements and the need for expensive and potentially harmful solvents and additives. Lastly, while not explored in this paper fully, it has been shown that these materials can be cycled within coin half-cells and future work will include a full characterization of their electrochemical characteristics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c01282.

Thermogravimetric analysis, differential scanning calorimetry, and data for the thermal characterization (DSC and DTA) of the materials (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank the Faraday Institution (Faraday Institution grant codes FIRG005 and FIRG006, project website https://relib.org.uk).

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Designing lithium-ion batteries for recycle: The role of adhesives

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A R T I C L E I N F O

Keywords: Design for recycle Lithium-ion battery Design for disassembly Adhesives Environmental impact

ABSTRACT

While electric vehicles are seen as an important tool in the decarbonisation of transport, pack and module architectures make disassembly and recycling slow and complex. Removal of physical fastenings such as clips, screws, welds and adhesives are the rate limiting factor in pack to cell disassembly. This study investigates the types of polymeric adhesives which are used in various battery components and shows how careful choice of components can speed up disassembly and circumvent the need for shredding and increase the purity and value of the recycled material.

1. Introduction

The demand for lithium-ion batteries (LIBs) in electric vehicles (EVs) has increased significantly due to their potential in decarbonisation of energy production. However, the scale of the projected electric vehicle market also indicates the exponential amount of battery waste that will be produced in the coming years, with conservative estimates stating that 1 million EVs have the potential to produce 250,000 tonnes of battery waste. As the market share of EVs grows, having surpassed 16 million in 2022, it is clear that the development of a circular economy model now whilst the scale of endof-life products is still manageable is essential to not only treat this waste but also recover the critical materials used in battery manufacturing. [1,2] Additionally, life cycle analysis (LCA) shows that recycling processes have the potential to reduce greenhouse gas emissions of the entire battery life cycle by 20 kg CO₂-eq/kWh_bc. [3] This industry will develop in concert with the processing of manufacturing scrap, and whilst in the early stages the recycling industry will have to contend with existing battery designs, in the future better designed batteries could unlock enhanced and more efficient recycling methods. A comprehensive roadmap for LIB recycling has recently been published, which summarises the key developments in LIB recycling, including design for recycle, and issues that still need to be addressed to establish a scalable recycling methodology capable of establishing a circular economy. [4].

The primary concern of battery design is to ensure safe and long battery performance with a high-power density to efficiently store electrical energy. Many of the design features currently employed make efficient and economic recycling challenging. Recycling has previously been seen as an end-of-pipe process, with little thought for end-of-life dismantling or processing. The approaches currently used are similar to those used in other waste recycling and primary metal extraction from ores. [1].

As with all complex devices, the components can be assembled using a variety of methods to contact distinct phases for structural integrity, strength and electrical continuity. These joining methods can either be physical (clips, screws, springs etc.), metallic (welds and solders), inorganic cements or organic adhesives. Unfortunately, the in-service properties are generally at odds with the end-of-life requirements. In service the joint needs to be durable and non-reactive whereas at endof-life it needs to be soluble or reactive. Most recycling processes start with a disassembly of the battery pack down to either module or cell level. From there, most physical and hydrometallurgical recovery start with comminution (shredding) to break joints and separate the different phases which results in cross-contamination between components and results in low value product streams. This is particularly an issue for

https://doi.org/10.1016/j.nxener.2023.100023

Received 1 March 2023; Received in revised form 19 April 2023; Accepted 10 May 2023

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Fig. 1. Examples of where structural adhesives are used within a battery pack using cylindrical cells.

polymeric and soldered components. A recent study on LIB recycling highlighted the difference in recycling economics depending on recycling method, geographical location and battery chemistry. [5] Dismantling the cell down into individual electrode materials as an alternative to shredding, can significantly improve economics and product purity but it is hampered by the complexity of the component joining techniques. [6] The cost of manual and automated disassembly has been estimated from the fixing and connector types found in a range of battery packs. [7,8] The study showed that economic recycling of battery packs requires automation which in turn depends on pack, module and cell design. Automated industrial disassembly has been argued to be a key enabler of a circular economy of EV batteries. [6] Current designs make disassembly complex due to the array of connectors used, the scale and packing of the cells and mechanical and chemical damage to the components during service. [9,10] It was noted in particular that the biggest barriers to disassembly were the number of screws when disassembling from pack to module and the number of welds and structural adhesives as well as the number of modules when going down to cell level. Fig. 1 shows some of the locations and application for polymeric adhesives used for in battery packs. For the structural and longevity reasons listed above, thermoset resins and unreactive fluorinated polymers have been extensively used throughout battery structure.

The logistics of moving waste is also important and it was shown that reducing transport and disassembly was important to the overall economics of recycling. [5] The geospatial configuration of a future recycling system will have a bearing on the impacts that arise at the end-of-life. The scale of the recycling plant is also important as are the hazard classification of end-of-life cells as it will affect the transportation costs if they are classified as hazardous. The configuration of technologies used for end-of-life processing, will have a bearing on the topology and structure of this future industry. Simple pre-processing that can take place near to the point of disposal may aid in reducing the quantity of material moved around the system, and the distances material must travel reducing the environmental burden of the end-of-life phase. Batteries that can be disassembled more easily close to point of disposal may unlock "hub and spoke" recycling models.

A variety of studies have investigated the technoeconomic assessment of shredding and disassembly. It was found that cost saving (with respect to using virgin material) of up to 20% could be achieved using shredding whereas cell dismantling could recover material with up to 80% cost reduction. [11,12] The advantages of shredding are that it rapidly reduces the active battery into a safer format. It is a process that is easily scaled, although the atmosphere around the shredder does need to be controlled. However, shredding does not separate aluminium from lithium metal oxide efficiently and attrition milling down to submm scale is required to get reasonable separation. [13] Studies have shown that impurities incorporated into recycled cathode material can significantly affect the performance of cells. [14] There are, however, caveats with these studies which, in most cases, have not considered the cost of disassembly and, for those which have, they do not dismantle beyond module level.

Design for recycle is not a topic which has been discussed in detail but a recent critical review highlighted many of the issues. [15] Design for disassembly has been discussed for removal of lithium ion batteries from PC laptops and although much simpler, issues of structural adhesives and fixing types are common with the automotive sector. [16] Product disassembly and material liberation is frustrated by the use of non-reversible adhesives in products. [17] In some cases, with thoughtful design and strategic placement, non-reversible adhesive bonds can potentially facilitate recycling, where they enable a "path of preferential breakage" which aids material recovery. The concept of disassembly sequence planning has also recently been introduced. [18] Moves to make the battery pack a structural element of the vehicle have led to an increased use in structural adhesives and permanent welds to increase pack rigidity. For example, the use of thermoset resins leads to the necessity for shredding rather than dismantling. A further disadvantage of thermosets is that they cannot be recycled and can only go to energy recovery. Thermoset resins are a high surface area foamed material, which also complicates separation and leads to entrapment of active material in streams destined for combustion.

Shredding has the disadvantage that the majority of electrolyte cannot be recovered and hydrolysis of salt can lead to the production of hydrofluoric acid (HF). It also leads to the necessity to scrub organic solvent from wastewater streams. While lithium is a minor value component, it is a significant mass component and lithium recovery efficiency is being targeted by battery legislation in many regions. In most cases the PF_6 anion has a significantly higher value although it is lost in most recycling processes.



Fig. 2. The proposed zigzag conformation for pouch cells. a) image of the dummy cell used in these experiments and b) the schematic diagram for the conformation showing placement of the adhesives.

The aim of this study is to demonstrate some simple design modifications that could be adopted to improve the ease of pack disassembly. Using dummy cells and modules the efficacy of disassembly is shown using, at times, robotic manipulation and the timings are compared to those proposed by Lander et al. [8].

2. Design for disassembly

Returning any device to its constituent components is fundamentally restricted by the numbers of interfaces and the methods chosen to join those interfaces. Recycling is made more challenging when dissimilar materials with incompatible properties are joined permanently using non-reversible adhesive bonds, making them difficult to separate. The three basic joining approaches; thermal welding, chemical adhesion and physical connection have implications for the cost, speed and permanency of the join and its subsequent release. The complexity of battery architectures has been highlighted in several recent reviews. [1,15,19].

There are numerous aspects of pack, module and cell design which can be adopted for simplified disassembly and recycling:

- Fewer, but larger cells
- Minimal use of thermoset adhesives
- Fewer fixing types
- Cells that are more easily opened
- Electrode binders that can be fully dispersed using water.

This article will review each of these ideas showing the extent to which each is viable. It will also analyse a case study currently being carried out to disassemble and recycle lithium iron phosphate (LFP) cells and the design aspects that can be assimilated from this process to other battery chemistries. The polymeric components can be split into two types depending on their applications:

- Extracellular: These hold the cells, modules, cooling components and the BMS together and are chosen primarily for their strength.
- Intracellular: These are chosen largely for their inertness and flexibility and maintain the active material in contact with the current collector.

2.1. Extracellular Adhesives

Disassembly tends to lend itself to form factors with larger amounts of battery material per cell, i.e. prismatic and pouch rather than cylindrical. This is for two main reasons: the time taken to open the individual cells and the mechanical separation of cells from each other in the module. The Tesla Model S P85 battery pack, for example, has 16 modules, containing a total of 7104 cells whereas the BMW i3 Mk 1 has 8 modules, each containing 12 cells (96 in total). Cell opening is viable with the latter as each cell opening process yields approximately 2 kg of material but with the former, less than 50 g of material are obtained. The disassembly of cylindrical cells is further complicated by their geometry, with active materials, foils and separators being spiral wound into a "swiss roll" like configuration, rather than the planar geometry of electrodes in pouch and prismatic cells.

In most pack and module designs currently used in the automotive sector, structural adhesives provide rigidity and strength to the assembly. Their use is logical, as they are inexpensive to apply and irreversibly provide the strength needed to minimise movement of cells during use. Most of the adhesives used are thermosets, based commonly on epoxides or polyurethanes. A recent critical review explained the possibility of using debondable adhesives which incorporate an element which enable depolymerisation or bulk delamination but it highlighted the difficulties of using heat, light or electrical potential as debonding stimuli in a battery pack. [19].

An important factor in the cost of LIB recycling is the complexity of pack disassembly. Manual disassembly is too slow and costly in many regions due to labour costs. It has recently been estimated that the manual disassembly time for many makes of electric vehicles are currently in the range 8–10 h. Automated pack disassembly down to modular level has been estimated to take 1–2 h and this is severely limited by the retooling of robots and the time taken to remove welds and glues. Most fixing methods are permanent, so servicing and end-of-life are not part of the pack design. Nine joining methods for metals in batteries have recently been identified, [20] and of these, only mechanical assembly (screws and clips) is seen as a process which makes disassembly easier, however mechanical fixtures add to the weight of the battery pack.

An important design for disassembly would be to avoid using structural adhesives as the only form factor imparting strength to a module or pack. One method to decrease the use of structural adhesives between cells could be to create a permanent link between pouch or prismatic cells and strategically place a small amount of adhesive at a point where selected directional movement could physically break the bond. One such arrangement could involve hinging the cells at alternate ends to create a zigzag conformation as shown in Fig. 2. This decreases the degrees of freedom that each cell can independently move in and generates levers between the cells. This could significantly decrease the amount of adhesive that needs to be applied to impart structural rigidity. If the properties of the adhesive are tuned correctly, separation of the cells into a linear configuration (Fig. 2) could be carried out effectively with programmed robots as only a simple extension of the design is required in the x-axis for the disassembly to occur.

2.1.1. Pressure sensitive adhesives

Pressure sensitive adhesives (PSAs) are a versatile class of viscoelastic materials which form bonds using initial pressure and flow, unlike conventional adhesives, which bond once they have hardened through a chemical or physical process. PSAs do not require additional agents such as heat, water, or solvents to activate. Due to this, the rheological properties of the adhesive must be adjusted specifically to their application. [21] The three main characteristics to be considered are ultimate adhesion, shear resistance and initial tack. Ultimate adhesion is the measure of the strength of the fully formed bond once the adhesive has set, shear resistance correlates to the adhesive resisting forces parallel to its surface and initial tack corresponds to the property that controls the instantaneous formation between the adhesive and adherend. [22] Contact adhesives are easier to apply than thermoset resins and are already used in small aspects of pack construction, their application over large surface areas make debonding slow and necessitates large volumes of solvents.

An investigation was carried out to compare the effectiveness of different types of commercially available PSAs including glue dots, double-sided tape, and Velcro. A peel test with tensile testing apparatus was used to simulate how a real module of cells using the zigzag conformation would be pulled apart. For this investigation two pouch cells of total weight 1.6 kg were created with a hinge between them by heat sealing a large pouch (41.5 \times 23.5 cm) in the middle. Initially no adhesive was used to set a base level for the different PSA's and to accurately compare their loading and extension which in turn corresponds to the energy required to break the connection. Then a PSA was applied onto the test sample and planted in our universal testing system. All adhesives were able to resist shearing motion in the z-axis and provided reasonable strength in the x and y axes as shown in Table 1.

As seen by the data in Table 1, double-sided tape is the strongest adhesive of the set closely followed by Velcro. Both provide viable solutions to holding a zig-zag-configuration cell together, however weight and spacing must be considered alongside the ease of removal of adhesive. In contrast to glue dots or double-sided tape, using Velcro increased the thickness of the sample design by nearly 35%, decreasing the power density. Additionally, a weight calculation was carried out to

Table 1

Comparison of the forces and associated energy required to open the modules using the zigzag conformation when different pressure sensitive adhesives are used.

Pressure Sensitive Adhesive	Average Load (N)	Maximum Load (N)	Energy Usage (J)
No Adhesive	6.02	9.76	2.12
Glue Dots	15.83	22.65	2.82
Velcro Strips	31.90	67.89	3.43
Double Sided Tape	58.67	103.77	4.49

evaluate each adhesive for the test sample, where it was found that Velcro contributes a relatively high amount of additional weight, while the glue dots contribute almost no weight.

Comparing the ease of removal of the adhesives, the double-sided tape was found to be the most difficult to remove, due to the sticky residue left behind. However, even this residue can be removed relatively easily with an acetone wash or by hand. Both Velcro and the glue dots did not leave residual material behind, thus making them a preferential choice in this respect as they would not require the additional removal step and therefore provide the simplest disassembly procedure. This is particularly useful in the area of pack or module repair and may decrease the proportion of cells being scrapped during production.

The amount of force required to separate the pouch cell design is also dependent on the position and orientation of the pressure sensitive adhesive. To demonstrate the applicability of using this approach, a dummy battery pack was constructed using 8 cells, each scaled down to 110×140 mm weighing ~193 g each, which was about 20% of the mass of a pouch cell that would be used in the Nissan Leaf. This was done due to limitations of the lifting capacity of the robots used in these tests. 'Franka Emika Research 3' robots were used to lift the 8-cell module from a box using two tabs. Two glue dots were adhered on alternate sides of the line of joined cells such that they could be aggregated into a zig-zag pattern. This approach enabled the ensemble to have mechanical strength but allowed some movement within the confines of the module container. The robot was able to lift the module contents and extend the string of cells into a straight line, as shown in Fig. 3, in only 15 s and this can also be viewed in video format. This automatic process could resemble how industry standard disassembly of a full battery pack could take place.

Alternative ways in which this could be carried out would be using strapping, commonly used in commodity transportation. These straps are usually made of polypropylene or polyester with either a thermal or metal crimped seal. This provides a physical join which is quicker to unfasten/refasten. Cutting this band would provide instantaneous cell release and simplify disassembly. Some test modules were made with single sided adhesive tape across the cell stack. These are reinforced tapes, but allow quick release when the tape is cut.

Cell opening can be easily automated with mechanical processes, however the material composition of the cell container has a significant impact upon which method can be utilised. A list of different methodologies that can be used are given in Table 3. The pouch cells are laminates of aluminium with polyethylene terephthalate (PET) and polypropylene (PP). [23] These are easily cut open with ceramic blades, leaving little residues or extra contamination. Other opening methods such as using lasers or plasma, produce heat during the cutting process,



Fig. 3. Images showing the stages of robotic module opening when the zigzag cell conformation is used. This process takes place over the course of 15 s.

but this can be optimised through fast, short pulses allowing for heat dissipation. [24] Any heat or sparks may ignite the flammable electrolyte. The sparking and heat removal may be further reduced with cooling fluids, which can also have a second benefit for passivation of the components as the cell is opened. [25] In addition, ultrasound could be utilised for pouch cell opening, as this tool can cut through multi-layers, and is used for materials which melt if exposed to heat, such as the laminate.

As mentioned, large format pouch and prismatic cells are preferred for this pack configuration due to their ability to stack easily within a module. The cells are stacked and glued together in the stack, with adhesive pads at the stack ends, to ensure rigidity in the module design. Pressure sensitive adhesives are already used in some aspects of battery construction in the form of double-sided sticky pads inside the module case, to maintain an intimate bond between the cell stack and the module case. However, the large contact area makes debonding problematic for disassembly. Removing the cell stack and separating the individual cells from their epoxy resin can take up to 2 h and require several litres of solvent. This disincentivises careful dismantling and the cells are usually shredded instead. Strategically placed, judicious use of adhesive pads may enable mechanical dismantling and also contribute less mass to the battery module. This could significantly improve the possibility for repair and reuse. While there may be concerns about the structural integrity of EV packs bonded in this way, this sort of approach could be ideal for static battery packs, where mechanical action is less of an issue.

2.2. Intracellular polymer binders

Once the cell is opened and the electrodes are separated, the next challenge is to separate the active material from the current collector and the polymeric binder. Polymeric binders provide adhesion and interconnectivity between electrode components, but they cause significant issues when left as a residue within battery waste streams obtained via shredding, known as the 'black mass'. Interactions between the binder and the other electrode components (active materials and additives) occur during slurry mixing via two mechanisms: direct binding, where the binder is physically adsorbed to adjacent particles forming interparticle bridges; Fig. 4a gives an example of this binding mechanism for a gelatin binder. The other mechanism is via indirect binding, where the polymer forms a chemically inert network which constrains the particles, seen in Fig. 4b for a polytetrafluoroethylene (ptfe) example system. [26] Sufficient dispersion of particles is also imperative in the formation of homogeneous slurries and is dependent on numerous factors, such as the density, flexibility and polarity of polymers, to promote electrostatic repulsion. Usage of appropriate solvents for a given polymer facilitates dissolution and aid in dispersion of particles within the slurries. For instance, the conventional polyvinylidene fluoride (PVDF) binder possesses a high dipole moment necessitating the use of polar solvents, such as N-methyl-2-pyrrolidone (NMP), to dissolve the polymer and resist flocculation within the electrode manufacturing process. [27] Binders also play an important role in electrochemical performance as key attributes of the binders such as flexibility and oxidation/reduction resistance, can dictate the degree of structural changes and chemical decomposition, impacting the amount of capacity fade and consequently the lifetime of these batteries. [28].

Recently, alternative water miscible binders have been the focus of research to reduce the usage of toxic solvents used in conventional electrode slurries, such as NMP. However, implementation of alternative binders is also essential to facilitate simplified and low energy separation of the electrode materials during battery disassembly. Fluorinated binders, such as PVDF, require high temperature pyrolysis $(> 400 \,^{\circ}\text{C} \text{ in air})$ to be removed, which produces toxic gaseous products such as HF during decomposition. [29] In-service breakdown products from PVDF, such as HF, are capable of reacting with transition metal oxides within the cathode active materials, decreasing their capacity. [30] These conditions could be significantly improved if an alternative binder is used in manufacturing. At present, the use of alternative binders has been largely limited to current and next generation anodes, with the most common example being carboxymethyl cellulose (CMC)/ styrene butadiene rubber (SBR), due to CMC being dispersible in water and SBR possessing good thermal stability, flexibility and adhesion. [31,32] Additionally, other water miscible binders, such as guar gum, [33] gelatin, [34] sodium alginate [35] and chitosan [36] have been investigated, showing similar properties to the CMC/SBR binders, with the possibility to be further enhanced via modification. [37-39] These water dispersible binder systems eliminate the need for the intensive conditions required for conventional battery separation steps, allowing facile separation of the active material and current collector, promoting the production of higher purity waste streams and simplifying subsequent recycling procedures.

Implementation of these alternative binder systems into cathode materials has been limited, as the resulting electrodes experience extensive cracking, and poor adhesion. The source of this cracking has been attributed to multiple factors, with corrosion of the aluminium foil considered to be the primary source. Aluminium corrosion is an issue in most industrial applications, however corrosion rates are limited, unless pH is significantly increased or decreased. [40].

$$2AI + 6 H^+ \to 2AI^{3+} + 3 H_2 \tag{1}$$

Water-based, positive electrode inks encourage the reactivity of the surface of the cathode materials, forming hydroxides which can dissolve in the ink, creating an alkaline slurry. If the pH is not controlled,



Fig. 4. Diagrams showing the two possible binding mechanisms for composite electrodes. The examples here show graphite particles as the active material. a) Direct binding - adsorption of particles to form interparticle bridges, b) Indirect binding - polymer network is formed and 'traps' active material particles.
the alkalinity of the slurry causes corrosion on the aluminium current collector, producing hydrogen gas via Eqs. 2 and 3. [41,42] Additionally, secondary sources of cracking can be brought about during the drying step, where the elimination and diffusion of the solvent can induce significant internal stress within the coatings, unless a relatively thin wet coating (thickness ca. 200 μ m) and low temperatures (20 °C) are employed. [43].

$$LiMO_2 + xH_2O \rightarrow Li_{1-x}H_xMO_2 + xLi^+ + xOH^-$$
(2)

$$Al + OH^{-} + 3H_2O \rightarrow Al(OH)_4^{-} + \frac{3}{2}H_2$$
 (3)

To replace PVDF, minimise NMP usage and avoid cracking in the electrode coatings, whilst enhancing cathode separation at the end-oflife, novel binder systems different from those currently being investigated for the anode may be required. Miscibility in water, if only partial, is still desirable in reducing the solvent and power requirements of end-of-life processing, but the cracking observed in manufacturing is a direct result of the use of water-based slurries. A possible compromise could involve use of co-polymerisation or blending of hydrophilic and hydrophobic polymers, allowing use of non-aqueous solvents during manufacturing, as well as a route for water-based electrode delamination processes to be used during battery recycling. An example of a possible system that could be employed uses starch and polyethylene to form a polymer blend that could be solubilised in deep eutectic solvents and was found to degrade in boiling water. [44] Usage of a polymer blend or co-polymer similar to this example would still result in a simplified electrode delamination process, similar to that observed when purely water miscible binders are used in the anodes. Incorporation of alternative binders into the cathode, as well as the anode, would simplify subsequent recycling procedures, minimise the use of harmful solvents, additives and high-power consuming processes, as well as attaining better recovery of the cathode active materials, which currently make up the majority of the value of end-of-life batteries.

2.3. Case study

End-of-life battery disassembly has been demonstrated on a commercial scale by the Swiss company Kyburz, who build light weight electric vehicles for private individuals, companies, municipalities, and delivery companies. Their vehicles are powered by LFP cells, and the recycling protocol is claimed to recover > 90% of the battery materials. These materials are then reused in secondary and tertiary applications, such as in 'used vehicles' ($\sim 85\%$ capacity) and power storage (between 65% and 85% capacity), respectively. [45] Kyburz uses cylindrical cells in a prismatic conformation, encased in a rigid steel casing. This recycling approach is only viable because no structural adhesives are used between cells, instead the internal components are held together via mechanical fixings, allowing for a simpler, albeit manual and more time-consuming, module-to-cell separation strategy. This approach is justified, given the relatively small sizes of the battery packs. It does, however, show that disassembly, rather than shredding, can be used if structural adhesive use is minimised.

Once the cells are separated, they are opened in an inert atmosphere, using a bandsaw to cut off the terminals and battery management system. The electrode roll is ejected from the casing by drilling a hole in the opposite end of the casing material and applying force using a compressed gas. The polypropylene separator between the electrodes is rewound vertically onto a spindle, allowing the anodes to fall in one direction and the cathodes to fall in the other. These electrodes are immersed in water, allowing a complete delamination. While no specific information exists about this process in the literature, this study replicated the process conceptually, where it was found that both the anode and cathode delaminated in under 30 min, with 100% recovery of material. In both instances, it is thought that intercalated lithium reacts slowly with water as there is evidence of gas evolution at both electrodes and the solution pH rises from 3.3 to 5.2 during delamination,

indicating lithium hydroxide formation (Eq. 3). It should be noted that the acidic starting pH arises from the formation of acidic species, such as hydrofluoric acid (equation 5), when the electrolyte reacts with the water. [46] Both observations can be related to the aqueous delamination solution leaching lithium from the active material and this provides a facile method for lithium recovery from the aqueous solution using ion exchange, precipitation, or evaporation of the solvent. The hydrogen forces the active layer to separate from the current collector, but it does not break apart the active material from the binder, so the active layer remains as a continuous phase. While the binder used in the batteries dismantled by Kyburz is unknown, thermal characterisation and IR carried out on commercial LFP cells have shown that they contain CMC/SBR as the binder for both anode and cathode. While this binder can be applied with water during slurry making, washing the electrodes with water is not sufficient to separate the binder from the active material. This residue is only fully removed with thermal treatment. An additional study, conducted by the authors compared the removal of CMC/SBR and sodium alginate (NaAlg) binders from a graphitic active material, after soaking in water and applying 10 s of high intensity ultrasound. Thermogravimetric analysis of the electrode material before and after ultrasound found that only 7.5% of the CMC/SBR was removed, while 76% of the NaAlg was lost. It should be noted that in the case of CMC/SBR, neither polymer was removed preferentially as a two-phase decomposition with the same mass loss ratio of 1:1 for each phase was seen before and after ultrasound processing. The study demonstrates the importance of novel intracellular binders, where the desired binders are soluble in water during both, manufacturing, and end-of-life processing, simplifying the disassembly procedure through further separation of the constituent parts of the battery materials.

While this approach seems applicable to this specific pack type and battery chemistry, there are aspects which could be applicable to other pack form factors. Most automotive packs have small cylindrical cells and, while the structural adhesives prevent segregation of the individual cells, they do provide rigidity and so a bandsaw approach could be used to open and separate cell contents from containers and prevent the cross-contamination observed in shredded materials.

3. Environmental impacts of utilising alternative adhesives

The use of alternative structural adhesives and electrode binders have been identified, both in this work and in previous investigations, to have a significant impact on simplifying battery disassembly. [19,39] Changes to cell design and the use of novel separation techniques, such as electrode ultrasonication, can form purer waste streams during endof-life processing. [47] In this section, the use of alternative adhesives and binders on the global warming potential and the processing capacity of recycling are compared.

A potential battery dismantling route is shown in Fig. S1. The impact assessments carried out in this work focus on the steps highlighted, as these will be mainly affected by the change in adhesive components. Environmental impact was assessed through global warming potential (GWP), which measures the ability of a greenhouse gas to trap heat within the atmosphere, relative to carbon dioxide, over the course of 100 years. [48] This was measured in reference to the IPCC 2013 impact assessment method, with the results given in kg CO₂-equivalents (kg CO₂-eq), which describes the amount of CO₂ that has the equivalent GWP of an emitted amount of greenhouse gas. [49] Modelling and calculations were completed using Umberto LCA + (v. 10.0) software and the Ecoinvent 3.7.1 database was used to acquire necessary data regarding the production and distribution of electricity and any solvent formulation.

3.1. Environmental impact of different structural adhesives during module opening

Table 2 shows that the choice of adhesive will influence the module opening time, which affects both the power requirements for module opening (measured in Wh) and the processing capacity. This study

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Table 2

Physical properties of the pressure sensitive adhesives used in this study including the dimensions and weight of the adhesives and the time taken for removal.

Pressure Sensitive Adhesive	Dimensions	Weight (g)	Average time taken to remove manually (s)
Glue Dot	0.3 cm radius	0.016	20
Velcro Strip	2 cm × 2 cm	0.434	25
Double Sided Tape	2 cm × 2 cm	0.052	50

assumes that the modules are opened with robots as shown in Fig. 3, technical information for the robotics was obtained from their data sheet and is listed in Table S1, along with other key parameters used in this assessment. [50] The reference scenario considered here is based on data for the Nissan Leaf module-to-cell disassembly previously assessed by Lander et al. This reference scenario permits comparison between the conventional cell design with structural adhesives, which are assumed to be epoxide based, and the zigzag conformation utilising alternative adhesives. [8] In the case of the alternative adhesives, the time taken for debonding was estimated based upon the manual debonding times in Table 2. When robots were used on cells joined with glue dots the time required for debonding reduced by 25%; it was assumed in these scenarios that the automation of disassembly provided a similar reduction in the time taken. Fig. 5 shows the GWP, energy usage and process capacity graphs obtained for these module opening scenarios and Table S2 gives the data behind this figure.

The first detail that should be noted from this data is the small GWP of this process, regardless of the adhesive used, as it has been shown in g CO₂-eq rather than kg CO₂-eq. In this instance, the low GWP correlates to the relatively low power requirements of the robots in opening the modules and the fact that these values have been determined based on the processing of a single module. The primary difference between the scenarios is the amount of time required to open up the module, which is dependent on the module design. As seen in Fig. 5, a significant reduction in GWP is observed between the reference scenario and the scenarios using the zigzag module design. The time discrepancy between the designs is related to the lack of physical fastenings like screws, simplifying the process required to dismantle the module and subsequently the amount of operation time the robots need for each module. The choice of adhesive used with the zigzag module is also important for minimising robot processing time and the associated GWP. All of the adhesives tested debond on the timescale of a few seconds. However, debonding of the glue dots was shown to be the quickest and hence shows the smallest GWP, at 250% lower than that of double-sided tape and 125% lower than the Velcro strips.

The reduction in disassembly time will not only affect the environmental impact of battery separation but can also facilitate a higher processing capacity for end-of-life battery treatments by improving the rate of battery disassembly. Processing capacity was estimated for each scenario based on their respective processing time and the amount of time required for the robot to reset and be ready to open another module, which was found to take around 20 s for the robots used in this assessment. Less processing time and a higher throughput of modules, paired with purer waste streams acquired through dismantling batteries over shredding, could have a significant impact on the profitability of recycling facilities, just through simple changes to module design and adhesive materials used in manufacturing.

3.2. Environmental impact of alternative binders during ultrasound delamination

The novel ultrasonic delamination technique proposed by Lei et al. was selected as the separation method in this study, to assess the effect alternative electrode binders have on battery disassembly. This has already been shown to have a beneficial technoeconomic analysis compared to many hydrometallurgical processes. Only delamination was assessed, so that the environmental impact of replacing the conventional binders can be emphasised. To obtain the input materials for this process from the opened module, the cells acquired in the previous step would have to be opened before the cell components, i.e. electrodes, separators, electrolyte and packaging, are separated into distinct waste streams, ideally via an automated process such as that demonstrated in the Kyburz process. [51] Cell opening and separation will also contribute GWP to battery recycling and future work will incorporate these steps into a full LCA study.

Two scenarios were investigated for electrode delamination, one being a reference scenario, using PVDF and CMC/SBR as the cathode and anode binders respectively. This scenario was compared to a hypothetical pouch cell using water miscible binder systems in both electrodes. It was assumed that the cathode binder was a hybrid system, like the example described in Section 2.3. Data related to the power, solvent and the time required to delaminate the electrodes was obtained experimentally. Table S3 shows the parameters assumed for this assessment. Electrode delamination of the cathode and anode will result in the formation of four distinct waste streams; the separated anode/ cathode active materials, and their respective current collector foils.

Fig. 5. Graphs showing the changes in global warming potential (a) and processing capacity (b) values corresponding to the opening of a battery module. The reference scenario assumes the use of a conventional module design and adhesives. The other data assumes the use of the zigzag module conformation with three different adhesive mechanisms.



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Fig. 6. Graphs showing the changes in global warming potential (a), energy usage (b) and GWP from solvent usage (c) values corresponding to the ultrasonic electrode delamination step. Reference scenario assumes the use of electrodes containing the conventional binders (PVDF and CMC/SBR). 'Water Miscible' scenario assumes the use of hypothetical electrodes containing water miscible binders.

The results from this assessment are given with respect to two of these waste streams, the anode and cathode active materials, given in Fig. 6, while all the data acquired, including that related to the current collector foils, is given in Table S4.

Fig. 6a shows a significant reduction in the GWP of ultrasonic delamination when alternative binders are utilised within the electrodes, with the recovery of both types of active material reducing their environmental impact. Fig. 6b and c show the power requirements and the GWP associated with solvent usage of ultrasonic delamination. This allows determination of whether the changes to the power output of the ultrasound or the solvents and additives used will reduce GWP the most. Since the anode already uses a water miscible polymer, CMC/ SBR, the reduction in GWP is not as extensive as that seen for the cathode, where PVDF is utilised. It is predicted that the only contributing factor to the reduction in GWP of the anode is from no longer requiring the solvent additives. This is because, unlike the binder assumed in the water miscible case, the commercial anode materials require additives, as well as water, to allow for complete and efficient delamination via ultrasound. Table S3 gives the type and amount of additives used for each electrode and the associated environmental impact data was retrieved from the Ecoinvent database. Although the impact that changing the anode material has on GWP is smaller than for the cathode, the elimination of additives and associated manufacturing routes can be significant, when dealing with the considerable amount of battery waste which will be seen in the coming years.

It has been shown in previous studies that while ultrasonic delamination is effective at removing the active material from the current collectors, the binders are still adhered to the active material particles, requiring high temperature processing in order to remove the binder. Anodes using CMC/SBR have the same issue as discussed in the aforementioned case study in this paper, where the use of NaAlg left significantly less binder residue when ultrasound is conducted using water as the solvent. This means that, as well as reducing the energy consumption of the disassembly processes, it also reduces the number of steps required, which would be beneficial to the overall economics and GWP.

Overall, when comparing the reference scenarios to the best alternative scenarios, i.e. using the glue dot and 'water miscible' scenarios, the % reduction in GWP in producing the separate anode and cathode material is 150% and 173%, respectively. It is also thought a similar reduction will be observed in processing costs of battery recycling, when comparing the reference and alternative scenarios. It is reasonable to assume that novel cell designs, new structural adhesives and water miscible binders will minimise recycling processing costs, with the aim to bring the cost towards the \$45 per pack suggested by Lander et al. [8].

4. Conclusions and future perspective

This study has shown that the biggest challenges faced by the emerging LIB recycling business is the complexity and diversity of the feedstock. The current LIB recycling market is dominated by small packs/cells from consumer electronics which is slowly being matched by automotive production scrap. Recycling will have to deal with legacy vehicles already on the market and new designs unlikely to come to end-of-life for at least 15 years. Future recycling plants will also need to deal with alternative electrode chemistries and structures. These include solid state batteries, nanostructured electrodes, [52] sodium ion batteries, [53] lithium sulfur batteries [54] and binder-less cathodes. [55] Some of these are more problematic than others, for example all solid state batteries (ASSBs) employ lithium anodes, which have adhesive properties that make traditional cutting methods challenging.

Table 3

Cell Opening Methods	Advantages/Disadvantages
Ceramic Blade	Mechanical cutting with ceramic blades, is simple. However, the tooling parts may require replacing frequently which adds to the cost and any HF released from the cell will exacerbate wear considerably. Cutting fluids can be used to reduce wear, and to improve throughputs.
Ultrasound	Suited to materials which cannot be exposed to heat, such as plastics which melt. Owing to lack of heat, this process may be the safest option for pouch cells.
Plasma	Requires electrically conductive materials and is often used for metals. However, a significant level of heat is produced that would need to be dissipated during long-term usage.
Laser	In most laser cutting applications, a robot is loading/unloading metal sheets to the bed of a laser cutting machine. Because lasers produce a large amount of heat, this could damage these robotics unless heat dissipation is carefully controlled.
Water Jet	High pressure water jets can be used for a wide variety of materials but may react with or cause contamination of the products if mixed with abrasive ingredients.

Conversely, binderless systems may lend themselves to simple ultrasonic delamination if the porosity is suitable.

Binders and adhesives are one of the most problematic aspects of recycling and the clear take home messages from this article are that the use of:

- larger cells,
- fewer structural adhesives such as epoxy resins,
- fully water dispersible binders,
- reversible physical connectors
- and alternative cell configurations

can all significantly simplify pack disassembly. The case study discussed in section 2.4 shows that cell opening and electrode separation can be achieved and coupled with intelligence-assisted predesign leading to purer product streams. [15,56] The range of opening techniques discussed in Table 3 show that this approach could be tailored to specific battery chemistries. These design aspects may be easier to apply to batteries used for different applications. For example, static packs used for energy storage experience negligible external mechanical stress so adhesion between packs components may be handled differently from those used in motorsport.

Improved battery design, particularly in vehicles results in easier repair and recycle and can results in improved brand reputation and increased residual values. Design for recycling has the potential to create environmental as well as commercial value. This is seen clearly in Section 3.0, where changes to both the adhesives and pack design used were found to have a significant impact on both energy consumption and processing capacity, minimising environmental impact and the cost of disassembly processes. Furthermore, emerging business models such as PAAS (Product as a service), which may aid in advancing circular economies, have the potential to unlock synergistic benefits for producers, if they become responsible for regenerating and recycling products once their initial service life has expired. We have argued that a clear legal extended producer responsibility (EPR) that balances the interests of end-of-life materials recovery with the requirements of second-life, [57] coupled with a servitisation model, [58] is the best route for promoting many of the goals outlined in this paper.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: ANDREW ABBOTT reports financial support was provided by The Faraday Institution.

Acknowledgements

The authors would like to thank the Faraday Institution (Faraday Institution grant code FIRG027, project website https://relib.org.uk) and the UKRI Interdisciplinary Circular Economy Centre for Technology Metals, Met4Tech project (EP/V011855/1) for funding.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nxener.2023.100023.

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