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QUILL
Quarterly Reports

May - July 2024

CONFIDENTIAL (up to July 2027)

Contents

QUILL Quarterly Report

May 2024 – July 2024

Name:	Oguzhan CAKIR		
Supervisor(s):	Professor Peter Nockemann		
Position:	PhD student		
Start date:	09/01/2023	**Anticipated end date:**	31/11/2026
Funding body:	Turkish Government (TENMAK)		

Magneto-Structural Properties of Boron-Containing Rare-Earth Magnets Synthesised Through Ionic Liquid Pathways

Background

Molecular nanoclusters constitute an intermediate state of matter between molecules and nanoparticles. The advantage of these materials is that, in contrast to conventional nanoparticles, they have a defined molecular structure that can exhibit cooperative spin-spin interactions, which might be used for magnetic high-density data-storage on a molecular level. We propose to investigate the synthesis of novel and interesting molecular cluster magnets using ionic liquid pathways; the aim is to achieve control over magnetic materials at cluster size with defined structures by using ground-breaking new synthetic methodologies.

Molecular cluster magnets provide a rich playground of different magnetic interactions in well-defined nanostructures, occupying the space between the quantum and classical world. Other interesting possibilities are clusters with antiferromagnetic or ferromagnetic intra-molecular couplings, which may exhibit bulk ferro- or ferrimagnetic interactions. Studying their physical properties contributes to our understanding of magnetic interactions in complex molecular structures. The use of ionic liquids allows for fundamentally different synthetic pathways resulting in compounds not accessible through conventional solvent-based synthesis.

Objective of this work

- Synthesise novel molecular cluster magnets with spin-cooperative behaviour using ionic liquid pathways.
- Understand synthesis of molecular cluster magnets through ionic liquid pathways including the formation mechanism
- The magneto structural properties of both the liquid precursor and the solid-state molecular cluster magnets as a function of varying syntheses conditions.
- Use the understanding of formation mechanisms and magneto structural property relationships to inform the design of further molecular cluster magnets.

Progress to Date:

I have completed several post-graduate training programs to enrich my research skills:

- Single-Molecule Magnets: Design, Measurement, and Theory by Prof. Nicholas F. Chilton at Manchester University

- Academic Writing and Referencing skills by Rachael Oniell, 8 weeks at Queen's University.
- "Training on Pure and the Research Portal" by Rebecca Clarke at Queen's University Solid State Pharmaceutical Analysis Methods Lecture by Professor Peter Nockemann, 12 weeks at Queen's University.
- Measurement and simulation of vibronic coupling in lanthanide complexes by Prof. Nicholas F. Chilton at Manchester University .

Additionally, I have conducted an extensive literature review on relevant topics including ionic liquids, molecular magnets, and magnetic ionic liquids. The key findings were compiled into a structured review and presented to Prof. Nockemann (see structure of the literature review below).

My project so far has focused on synthesising and characterising novel boron-containing rare-earth molecular magnets using ionic liquid pathways. The work is divided into three main stages:

1. Synthesis and characterisation of ionic liquid precursors.
2. Synthesis and characterisation of rare-earth coordination complexes.
3. Synthesis and characterisation of final boron-containing rare-earth magnets.

I have successfully completed stages 1 and 2, with promising results. The cluster compounds studied feature three-dimensional acetate and oxalate frameworks housing arrays of rare-earth metal ions; their magnetic properties derive from the magnetic moments of the rare-earth ions coupled via oxygen bridges. I am currently optimising the experiments for stage 3 to obtain the target materials. The next phase will involve investigating the magneto-structural properties of the synthesised compounds in detail. Overall, the project is progressing well in line with the initial timeline.

I presented QUILL conference through a slide presentation and poster in March. In addition, I will present a poster the next QUILL conference in 2nd of September.

I applied for my annual progress review. I will present my work at the upcoming differentiation meeting.

Here is the proposed structure of a literature review on the topic of boron-containing rare-earth magnets synthesised through ionic liquid pathways:

Introduction

- Background on rare-earth magnets and their importance.
- Brief overview of conventional synthesis methods and their limitations.
- Introduction to ionic liquids and their potential as solvents for inorganic synthesis.

Ionic Liquids

- Properties of ionic liquids relevant to inorganic synthesis (negligible vapor pressure, thermal stability, etc.)
- Use of ionic liquids as solvents in inorganic chemistry.
- Types of ionic liquids suitable for rare-earth and boron chemistry.

Molecular Magnets

- Fundamentals of molecular magnetism.
- Important classes of molecular magnets (e.g. single-molecule magnets).
- Strategies for designing/improving molecular magnets.

Synthesis of Molecular Magnets

- Common synthetic techniques.
- Use of conventional solvents and limitations.
- Emerging non-conventional techniques (hydro/solvothermal, microwave, mechanochemical, etc.)

Rare-Earth Borates

- Structural motifs and magnetic properties of rare-earth borates.
- Current synthetic approaches to rare-earth borates and limitations.
- Characterisation techniques for structure and magnetism.

Ionic Liquids for Rare-Earth Borate Synthesis

- Recent examples demonstrating utility of ionic liquids.
- Structures and properties of rare-earth borates achieved through ionic liquid synthesis.
- Proposed mechanisms for ionic liquid synthesis and advantages.

Outlook and Conclusions

- Summary of key points and current state of literature.
- Remaining challenges and unanswered questions.
- Proposed directions for future research.

QUILL Quarterly Report

May 2024 – July 2024

Name:	Aodhán Dugan		
Supervisor(s):	Prof P Nockemann, Dr O Istrate & Dr P Kavanagh		
Position:	PhD Student		
Start date:	Oct 2023	**Anticipated end date:**	Sep 2026
Funding body:	Shell/DfE		

Enhancing Vanadium Redox Flow Battery Performance with Hydrothermally Grown Polyoxometalate Nanoparticles on Graphite Felt

Overview

Due to the contribution non-renewable and unsustainable fossil fuels have made to the global climate crisis, an urgent demand for clean, renewable energies has emerged. Renewable energy sources such as wind and solar while abundant remain challenging to integrate into the large-scale energy grid due to their intermittent nature. This has created major interest and investment in large-scale energy storage technologies, in which vanadium redox flow batteries (VRFBs) are among the most promising. The potential offered by VRFBs can be owed to several attractive features such as high durability, relative safety, high round-trip efficiency along with a system design that decouples the power (cell size) and energy (reservoir size) components, allowing for scalable design based on application needs. Although this technology has much promise, its relative high cost still restrains further industrial application. Among other factors, low power density creates a demand for more electrochemical stacks which vastly increases the cost due to the price of cell components e.g. Nafion|r N-117, 0.180mm thick ion exchange membrane = £9.74/cm^2 (Fisher scientific). Improving power density is therefore an integral aspect of pushing VRFB toward wide-spread application. As a key component of the system, the physical and electrochemical properties of the electrode have a decisive impact on the functionality and performance of the battery. The critical role the electrode plays in the operation of the VRFB is that it provides the reaction surface for active species to undergo redox reactions, thereby is the active sit for the storage or release of energy. At present, the most commonly used electrode material for VRFB electrode is polyacrylonitrile (PAN) based graphite felt (GF) which has the advantage of high conductivity and high chemical stability in acidic media. However, poor electrochemical activity towards the vanadium half reactions spawning from the material's inherent hydrophobic nature along with lack of active centres are key challenges in increasing the batteries power density, prompting modification studies which aim to improve the fibres of the GF through surface functionalisation. Several approaches have been taken including intrinsic treatments (heat, plasma, acid/base), carbon catalysts (graphene, fullerene, carbon-dots), metal catalysts (Ag, Bi, Sn) and metal oxide catalysts (PbO_2, SnO_2, WO_3), while show improvements suffer drawbacks limiting their wide-spread application. Recently, polyoxometalates (POMs) have been widely studied in the field of electrochemistry, particularly energy storage systems but have not yet been explored as electrode surface catalysts for RFBs.

Objective of this work

This work aims to improve the VRFB system by increasing the battery's power density, which can be achieved through electrode surface modification. POMs have been identified as potential catalysts for this purpose and will be loaded onto the electrode surface via a hydrothermal method.

Work to date

The POM tetrabutylammonium hexamolybdate $[(n\text{-}C_4H_9)_4N]_2[Mo_60_{19}]$ has been successfully synthesised and characterised using FTIR and Single-Crystal X-Ray Diffraction. Hydrothermal method was used to deposit the compound onto the GF by heating at 150 ^oC for 8 h in 0.1 M $[(n\text{-}C_4H_9)_4N]_2[Mo_60_{19}$ solution. The result was total saturation of fibres in crystals which hindered the electrochemical performance of the felt in posolyte. To address this issue, the treatment solution concentration was reduced to 0.0005 M and both temperature and time of treatment method were reduced to 120 ^oC and 5 h, respectively, following GF activation via heat treatment at 500 ^oC for 5 h. SEM imaging allowed for the observation of nanoparticles grown to 47 nm on average (*Figure 1)*. The resulting GF were subject to contact angle measurement using both posolyte and negolyte which exhibited limited physical interaction improvements and instant adsorption, respectively, indicating that while the GF modification does not improve the physical electrolyte-electrode interaction in the positive side, it substantially improves this effect on its negative counterpart (*Figure 2a-b*). Modified GF were subjected to CV analysis in a classic three electrode set up which included 1 cm x 1 cm x 0.5 cm pieces of pristine GF (P-GF), heat-treated GF (H-GF) and POM modified GF (POM-GF) as working electrodes, H-GF as counter electrode and Hg/HG_2SO_4 as reference electrode. The scans were carried out in 50 mmol V^{2+} and VO^{2+} in 2 M H_2SO_4 at a scan rate of 10 mV/s. Although no improvements were observed for the positive half reaction, an increase in peak anodic and cathodic current densities of 91 % and 142 % were observed in the negative side when comparing POM-GF to H-GF respectively, suggesting an improvement in electrochemical activity of the GF (*Figure 2c-d*).

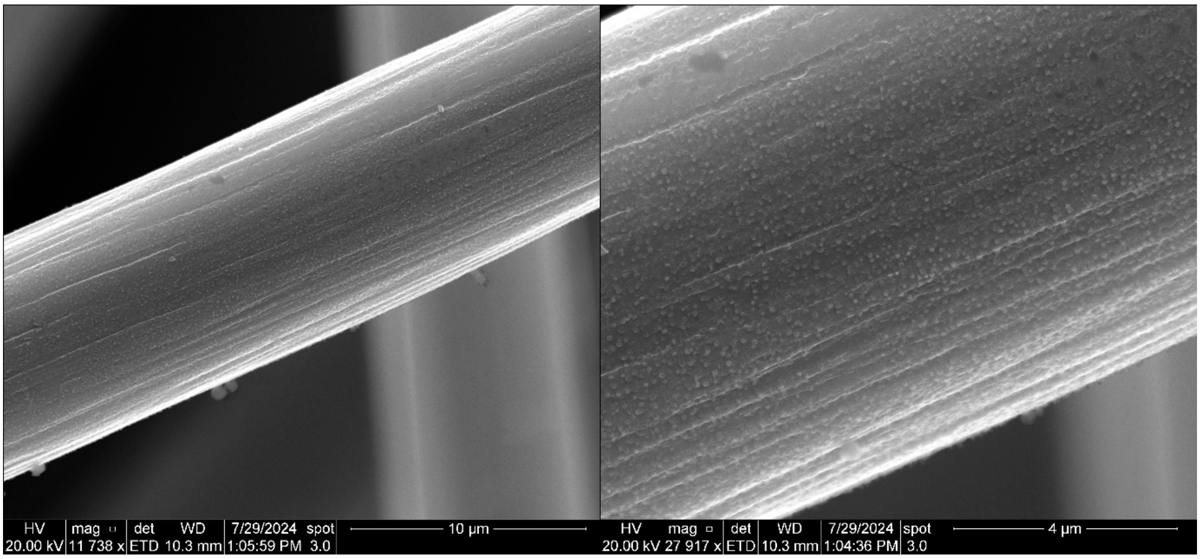

Figure 1 – SEM images of GF treated in 0.0005 M $[(n\text{-}C_4H_9)_4N]_2[Mo_60_{19}]$ at 11738 x and 27917 x

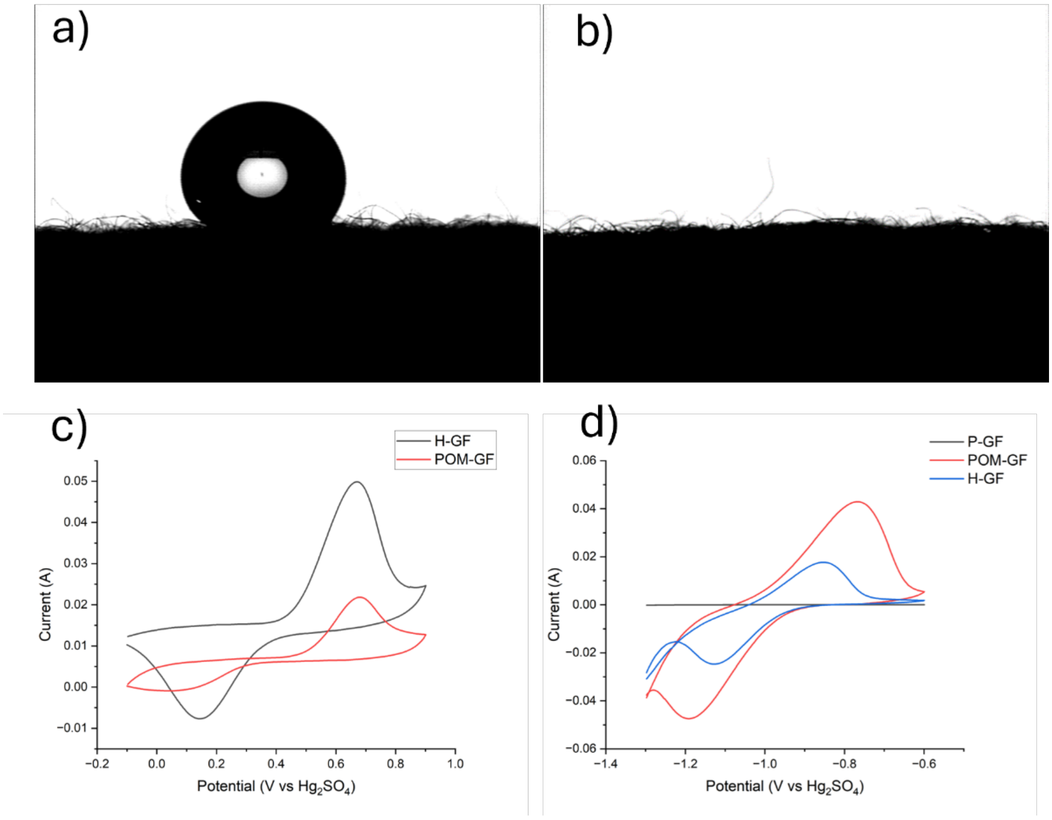

Figure 2 – a) contact angle measurement of POM-GF using 50 mmol VO^{2+} in 2 M H_2SO_4 b) Contact angle measurement of POM-GF using 50 mmol V^{2+} in 2 M H_2SO_4 c) Cyclic voltammograms of H-GF and POM-GF in 50 mmol VO^{2+} in 2m H_2SO_4 at a scan rate 10 mV/s d) Cyclic voltammograms of P-GF, H-GF and POM-GF in 50 mmol V^{2+} in 2m H_2SO_4 at a scan rate 10 mV/s

It is suggested that the improved physical interaction of the electrode in negolyte solution improved the electrochemical activity of the GF by allowing active species increased access to the surface, while also providing more electrochemical active sites in the form of POM-nanoparticles.

Conclusion and future work

To conclude, reduced concentration accompanied by pretreatment of GF and decreased reaction time and temperature supported the growth of nanoparticles. POM-GF showed no electrochemical improvements in posolyte but improved the performance in negolyte, through improved electrode/electrolyte interaction and increased number of active sites. Future work will focus on the modified electrode’s repeatability, stability and overall cell performance, before identifying a variety of other POMs as potential loading materials.

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May – July 2024

Name:	Nia Foster		
Supervisor(s):	Dr P Kavanagh & Prof P Robertson		
Position:	PhD Student		
Start date:	October 2023	**Anticipated end date:**	September 2026
Funding body:	Department of Economy		

Electro-Photo Generation of Highly Reducing Radical Anions for CO_2 Activation

Background

Electrochemistry has recently been a huge area of interest in chemistry, being used in areas such as synthesis, batteries, and analysis. It is commonly used in homogeneous redox catalysis, where a voltage is applied across the electrochemical cell, allowing for electron transfer between the electroactive substrate and the electrode.

The focus here is on electrochemical homogeneous redox catalysts that carry out reductions. The issue is that it can be difficult to get a catalyst to a high enough energy level to be able to reduce difficult substrates such as CO_2. We require a technique that can raise the catalyst to a higher energy level while surpassing these limitations within the cell. Ideally, we want to avoid additives that are harmful chemicals and that cause more waste, therefore we turn to photochemistry to try and excite the catalyst to a higher energy level.

Studies on homogeneous electrophotocatalysis emerged around the late 1970's, with Moutet and Revardy's research into using phenothiazine as an oxidising agent being one of the most popular examples. Interest in electrophotocatalysis continued through the 80's however interest dwindled. It wasn't until 2019 when academics such as Xu, Stahl, and Lambert sparked renewed interest in the area with their papers on Mes-Acr, iodide ions and TAC, respectively.

As we noticed a gap of knowledge in previous research, we have turned our attention to compiling research on electrocatalysts. Previously, many research papers used specific catalysts without explaining why or how each catalyst is the most effective. The first study carried out involved testing a range of electrophotocatalysts using cyclic voltammetry, and finding three properties: their redox potential, diffusion coefficient and their heterogeneous electron transfer constant. After completing this study, we noticed a discrepancy between the figures – some were two orders of magnitude larger than others. Looking at previous papers, we could see that there didn't seem to be much reproducibility between figures for the same catalyst in the same electrolyte from one paper to another, so we realised that there is a need to find these properties under a defined set of conditions to aid comparison.

Objective of this work

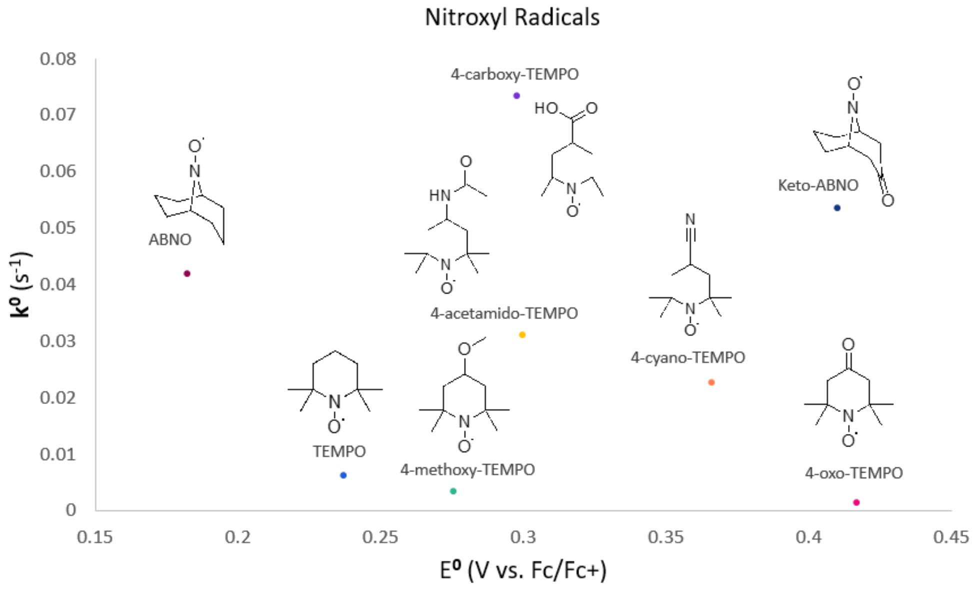
The plan is to study a series of homogeneous redox electrophotocatalysts, specifically reductive electrophotocatalysts. By activating these catalysts though applying a negative potential and exciting them using light, they will have a very high energy that ideally will be used to reduce more difficult substrates such as carbon dioxide or nitrogen. Ideally, we want to remove carbon dioxide from the atmosphere and turn it into a more value-added fuel.

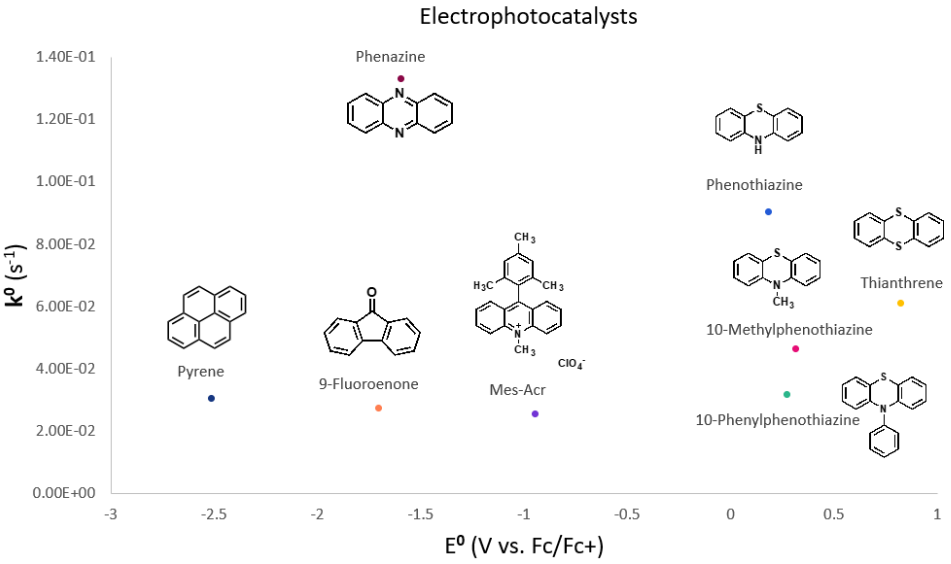
Progress to date

The first part of my PhD that I had been working on is categorising a series of homogeneous redox electrophotocatalysts that have previously been mentioned in papers. I wanted to compare them all and be able to find their redox potential, their diffusion co-efficient and their electron transfer constant.

However, we have noticed that there seems to be a lot of disparity between values reported in papers on these parameters, and that they are difficult to reproduce. We believe they are not measured as accurately as they could be, and that alternative methods should be used. Previously, only cyclic voltammetry has been used to find only the redox potential, but by using rotational disc voltammetry we are able to produce more accurate values for the apparent rate constant and diffusion coefficient. We have also noticed that correcting for resistance and baseline current makes a big difference, so by employing all these factors we are ensuring we get the most accurate and reproducible results. Experiments are currently being carried out on a range of electrocatalysts to be able to provide a catalogue of catalysts and values for myself and other electrochemists to use.

The experiments are almost completed, and the results will be displayed like the examples below. This makes it very easy to compare one catalyst to another, being able to quickly see which catalyst has a higher electron transfer constant at a certain redox potential:





Conclusions and future work

As most of these experiments have concluded, the immediate next step is to analyse all of the results and ideally start writing a paper that categorises these catalysts based off the three properties previously mentioned, which will hopefully be very useful for myself or other electrochemists in the future.

Further on from that, if I am to continue in the electrophotochemistry direction, the catalysts will need to be tested under blue or UV light, to observe whether the catalyst is indeed a successful photocatalyst as well as an electrocatalyst, and to see how much more effective the catalyst is once photochemically excited.

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May – July 2024

Name:	Michael Gamble		
Supervisor(s):	Dr Istrate, Prof Peter Nockemann & Dr Arredondo-Arechavala		
Position:	PhD Student		
Start date:	February 2024	Anticipated end date:	February 2027
Funding body:	Shell/DfE		

Activation of Carbonaceous Electrode Materials for Improved Performance of Redox Flow Batteries

Background

The increasing energy demands of a rapidly growing global population and anthropogenic climate change have resulted in an escalating interest in renewable energy like wind and solar power. However, such sources of renewable energy are inherently intermittent and cannot be relied upon to produce constant power analogous to fossil fuel-based technologies. Therefore, energy storage systems represent an important and complementary technology to overcome this significant shortcoming. Among the storage systems available, redox flow batteries (RFBs) are a promising technology owing to their long lifecycle, deep discharge tolerance and low environmental impact. Within this battery system, chemical changes to the active species within the electrolyte are the mechanism for the storage and release of electrical energy. Furthermore, unlike other secondary batteries, the active species are stored separately from the location of power conversion. This allows for the independent scaling of energy and power within RFB design.

Despite the inherent advantages of the RFB, the relatively low power density and high fixed costs of this technology compared to other energy storage systems mean that it struggles to penetrate the commercial marketplace. To address this, the electrocatalytic performance of the anode and cathode needs to be improved. This is because, as the location of vanadium ion redox reaction during charge and discharge, they have a major influence on the power losses and energy efficiency of the battery, which in turn determines required stack sizes and the production costs of the VRFB. Graphite felt (GF), a type of porous carbon fabric electrode, is commonly employed as the electrodes within a VRFB due to its affordability, stability and good conductivity. However, it suffers from poor kinetic reversibility, small specific surface area (< $1m^2g^{-1}$), low wettability and limited electrochemical activity with the vanadium ions utilized. In response to these issues, a large variety of treatments have been applied to GF by the scientific community. For example, chemical etching, metallic modification, metal oxide doping, compression, non-metal doping and carbonous nanomaterial decoration have been employed on GF in order to activate it.

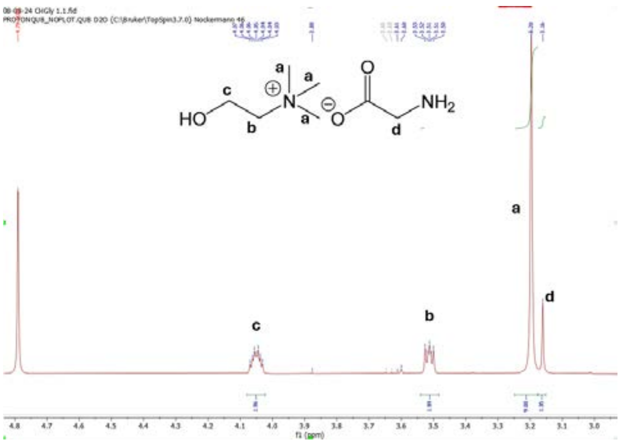
A major part of this research will be to assess the ability of protic ionic liquids (PILs) to improve the performance of GF. Specifically, PILs will be utilised to dope the surface of GF with nitrogen-doped carbon (NDC) using a facile pyrolysis methodology. Another aspect of this work will be to investigate the effects of electrode compression on the performance of GF.

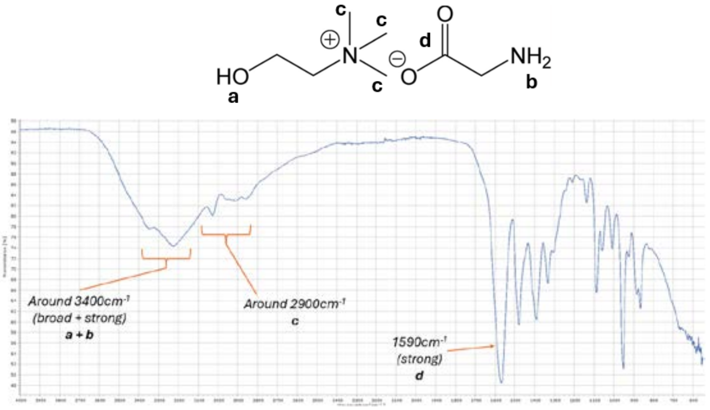
Objective of this work

The overall aim is to increase the power density of RFBs through the activation of graphite felt electrodes. The avenues of activation that will be investigated are decoration with nitrogen-doped carbon materials created from the protic ionic liquid choline glycine ([Ch][Gly]) and electrode compression.

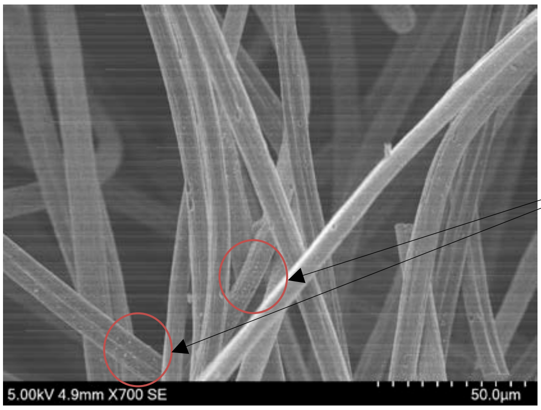
Progress to date

Since June 2024, there has been significant progress towards decorating the surface of GF with the NDC formed through the pyrolysis of [Ch][Gly]. The first major piece of progress is that the methodology that has been used in order to synthesize [Ch][Gly] has been changed. This is because, using the previous methodology, it was very impractical to remove the excess glycine from the final product due to the small quantities of ionic liquid that were being created. Therefore, a new one-pot synthesis methodology has been chosen where this was not an issue. After choosing this new methodology and conducting more rigorous purification steps, [Ch][Gly] was resynthesized in a more concentrated form. Its synthesis was confirmed through the use of NMR and FTIR. The images below present the results generated from the use of these characterisation techniques.





After the successful synthesis of [Ch][Gly], it was coated onto thermally activated GF utilising the drop casting technique. Specifically, this involves immersing thermally activated GF and [Ch][Gly] in a methanol solution. The methanol was then allowed to evaporate off and this resulted in the GF being coated with [Ch][Gly]. After drop casting, the GF coated with [Ch][Gly] was pyrolysed at 800 degrees celsius for 2 hours. The pyrolysis was conducted to convert the [Ch][Gly] to nitrogen doped carbon while it is coated on the surface of GF. After the pyrolysis was completed the following SEM image was taken,



Potentially the nitrogen doped carbon created from [Ch][Gly].

While this image in no way confirms the presence of nitrogen doped carbon on the surface of GF, it does it least provide an encouraging result that some may have been decorated on its surface.

As mentioned previously the drop casting methodology made use of thermally activated GF. The reason for this is so that the graphite felt was hydrophilic enough to be immersed within methanol. Specifically, GF was thermally activated at 600˚C for 5 hours. Proof of improvement of wettability was shown through the use of contact angle testing.

Conclusions and future work

Over the last three months, there has been a consolidation of the specific methodology that will be utilised in order to decorate the surface of GF with the nitrogen doped carbon created from [Ch][Gly]. Additionally, although it needs more rigorous confirmation, recent SEM images do reveal that nitrogen doped carbon may have been created on the surface of GF. There are two main goals for the next three months of research. The first is to continue using the created methodology and confirm that the NDC created from [Ch][Gly] has been decorated on GF. The second goal is, assuming successful decoration, to assess the improvement in GF performance through the use of techniques such as CV, EIS and flow cell testing.

QUILL Quarterly Report

May – July 2024

Name:	Edwin Harvey		
Supervisor(s):	Dr Oana Istrate, Prof Peter Nockemann & Dr Stephen Glover		
Position:	PhD Student		
Start date:	February 2022	**Anticipated end date:**	August 2025
Funding body:	Department for the Economy		

3D Printing for Renewable Energy Applications

Background

Redox flow batteries (RFBs) are promising candidates for grid-scale energy storage and stationary energy storage applications. They have a longer cycle life than lithium-ion and can use cheaper, safer, and more environmentally friendly electrolytes. Such systems are becoming more important as we rely more on intermittent renewable energy, such as wind and solar, as we move towards reaching net zero by 2050 (UK govt target).

The RFB design has not changed much since their inception in the 20th century (e.g. vanadium RFBs were invented in 1986 at the University of New South Wales, Australia). Electrodes are still typically made using carbon felt as these have good electrical conductivity, electrochemical activity, and are mechanically and chemically stable. However, using carbon felt as an electrode material limits cell design and is associated with a high interphase electrical resistance. Additionally, for flow-over electrode designs, flow channels must be machined into graphite plates which is complex and expensive. 3D-printable electrodes may offer a greater design freedom where, for example, flow channels can be printed as part of the design, and porous and solid elements can be combined.

Graphene nanocomposite materials may be able to replace graphite and carbon felt as an electrode material. Possible 3D-printing technologies for this material are fused deposition modelling (FDM), and stereolithography (SLA). FDM uses a heated thermoplastic filament which is extruded out of the printer nozzle, following a pre-calculated path to manufacture the part layer by layer. Graphene based nanocomposites have been printed using FDM but often suffer from agglomeration of graphene due to extruding conditions. SLA uses a liquid resin which is cured using UV light at the desired locations, also building the part layer by layer. SLA may offer improved graphene dispersion compared to FDM.

Objective of this work

To utilize multifunctional nanocomposites to redesign redox flow cell for improved energy efficiency

Progress to date

Initially, I spent time reading literature and planning my PhD by splitting it into work-packages that each last a few months. My first work-package is focused on manufacturing a 3Dprintable RFB material utilising carbon nanofillers. After analysing the properties of various polymer matrices, I have decided to focus on acrylate-based monomers that can be polymerised in-situ with graphene. This is because various papers have shown this method to produce high electrical conductivity and excellent graphene dispersion.

During initial experimental work graphene oxide (GO) was synthesised using a modified Hummers' method. Following this, seven polymer/graphene nanocomposites were manufactured using SLA 3D-printing containing GO and graphene nanoplatelet (GNP) fillers. Nanofillers and nanocomposites were then characterised using FTIR, Raman spectroscopy, X-ray diffraction, tensile testing, and electrical testing. A literature study and experimental work were submitted as part of my differentiation which was completed in November 2022.

Since November 2022, I have been focused on manufacturing and modifying graphite powder and developing my characterisation skills. I have been undertaking an in-situ polymerisation method to produce high electrical conductivity nanocomposites which have the potential to be used as a 3D-printed electrode material.

Since February 2023, I have been focusing on a latex mixing method for producing graphite oxide nanocomposites. This has involved testing different mixing methods and adding salts to coagulate the particles into a nanocomposite.

Since May 2023, I have focused on refining the latex mixing method to produce mouldable graphene oxide composite materials. I have shaped the composite material and undertaken CV electrochemical measurements in a vanadium electrolyte which shows promising results. I've also been performing a full characterisation of the composite material (TGA, DSC, Raman, FTIR, etc.) and writing up the info for a paper submission.

Since August 2023, more detailed electrochemical characterisation has been undertaken. Oxygenated groups on graphene nanocomposites were shown to offer enhanced electrode activity in vanadium redox reactions. The focus of the project has moved back to resin 3D printing (e.g., SLA or Digital Light Processing). Using the synthesised graphite materials (expanded graphite, graphene oxide, and pristine graphene), different nanocomposite architectures have been produced using resin 3D printing. Challenges producing nanocomposites include dispersing fillers in resin, keeping viscosity at an appropriate level for printing, and final mechanical properties.

Since November 2023, we have been developing compression moulded flow fields for RFBs. Firstly, a composite material of PMMA/graphite was synthesised using methods refined through the PhD. Using a mould produced through CNC manufacturing, flow fields were successfully compression moulded with different densities. The compression moulded flow fields are electrically conductive and can be produced in similar designs to commercial machined flow fields.

Since February 2024, testing related to the fundamental properties of the synthesised nanocomposites performed (e.g., Raman Spectroscopy, X-Ray diffraction analysis (XRD), Electrical conductivity testing, Cyclic voltammetry (CV)). Have found a way to enhance the surface electrochemical properties of polymer nanocomposites by fixing oxygenated graphite nanofillers. Work advanced on shaping of nanocomposites using CNC compression moulds. Thesis and publication writing.

Since May 2024, focus has been on planning thesis chapters and remaining experimental work. I’ve set out four work packages/chapters for my thesis: WP1 - Nanocomposite synthesis via latex sonication, WP2 - Moulded nanocomposite characterization, WP3 - Nanocomposite shaping via 3D printing, WP4 - Component battery testing.

Recent experimental work has included electrochemical testing (CV and EIS) in vanadium electrolyte on moulded PMMA/graphite samples. PXRD and Raman spectroscopy has been used to analyse graphene exfoliation in nanocomposite powders.

Redox flow cell architectures have been manufactured using compression moulding. Galvanostatic Charge/Discharge (GCD) testing has shown promising results of the assembled cells, although work is ongoing to find cause of capacity fade.

Conclusions and future work

Synthesised polymethyl methacrylate (PMMA)/expanded graphite composite material shows promising electrical and electrochemical properties, as well as being shapeable into cell architectures. Future work includes implementation of the material in FDM 3d printing, and continuing charge/discharging testing of assembled redox flow cells.

QUILL Quarterly Report

May – July 2024

Name:	Aloisia King		
Supervisor(s):	Prof John Holbrey & Prof Małgorzata Swadźba-Kwaśny		
Position:	PhD student		
Start date:	Oct 2021	**Anticipated end date:**	May 2025
Funding body:	EPSRC		

Manipulating Cation Lewis Acidity to Create Functional IL Systems

Background

Frustrated Lewis acid/base pairs (FLPs) are potential metal-free alternatives to platinum group metal catalysts and have been shown to activate hydrogen for hydrogenation chemistry [1]. Typical examples of FLPs that have been studied are combinations of a sterically hindered bulky phosphine Lewis base paired with a strongly electrophilic Lewis acidic susbstituted borane. While many of the advances in FLP chemistry have sought to exploit these bulky phosphine/borane pairs, less attention has been given to alternative acid/base pairs although examples with non-boron Lewis acid FLP components are known including N-alkylacridinium cations which have been show to exhibit FLPs chemistry when paired with lutidine (2,6-dimethylpyridine) as a base [2].

Objective of this work

The goal of this research is to develop organic FLPs (eliminating the need for group 13-based Lewis acids) within an intrinsic IL medium in which, ideally, the potential catalyst concentration in the liquid is maximised and enables reaction intensification creating greener, sustainable chemistry through facile synthesis and replacement of both conventional solvents and platinum group metal catalysts.

Progress to date

Five *N*-alkyl-acridinium salts and *N*-protonated heterocyclic ionic liquids, as precursors for FLP studies, have been successfully synthesised and fully characterised. *N-alkylated N-a*lkylacridinium *bis*{trifluoromethylsulfonyl}imide ([R-Ac][Tf_2N]) salts synthesised are highly soluble in H-lutidinium and H-picolinium *bis*{trifluoromethylsulfonyl}imide ([H-lut][Tf_2N] and [H-pic][Tf_2N]) ionic liquids. This contrasts with the reported poor [2] and limiting solubility of *N*-methylacridinium salts in organic solvents. Since the last report, I am still preparing a manuscript for publication and have written the bulk of one thesis chapter. Additionally, our proposal to carry out neutron scattering studies on acid/base association in the N-methylacridinium bistrifylimide/lutidine ionic liquid FLP has been successfully granted beam-time is ISIS, RAL requiring synthesis of deuterated N-alkylacridinium salts and lutidine. I have began my studies into the deuteration of the entire system. During the month of June, I completed and submitted my application for Associate Fellowship of the Higher Education Authority. Also, ongoing investigations are being conducted on 3,5-dicyanopyridinium analogues of the N-alkylacridinium Lewis acid components of FLPs and I have devised methods to synthesis these molecules successfully. We anticipated that this set of molecules may be able to be used as alternative cations (within an FLP system), due to their similar hydride ion affinity to that of the dihydromethylacridinium molecule [3]. These N-alkylated-3,5-dicyanopyridinium cations should also feature innate ability to act as IL based charge transfer materials, extending previous work within QUILL (Hardacre, Holbrey, Mullan) on cyanopyridinium IL charge transfer complexes [4]. CT forming complexes of ILs with electron-rich donor aromatics, We also have decided to revisit a range of 4-cyanopyridinium bistrifylimide that have been examined by the Group in the past as CTMs, when paired with 1-methylnaphthalene. The aim of this work is to try and develop a deeper understanding of the charge shuttling/ transfer mechanism between these ILs and 1-methylnaphthalene via electrochemical impedance spectroscopy (EIS), collaborating with Dr. Josh Bailey. The robustness of the electrochemical cell design required for EIS measurements has been improved, allowing reliable temperature control, and EIS conductivity studies on cyanopyridinium ILs and IL/aromatic CT complexes is underway. I have conducted the EIS studies on the C_1CNPyr[NTf_2] and C_2CNPyr[NTf_2] ILs and also the mixtures of these ILs with 1-methylnaphthalene. I have prepared the C_3CNPyr[NTf_2] and C_4CNPyr[NTf_2] ILs and will be carrying out the EIS of these ILs and their mixtures with 1-methylnaphthalene in August.

Conclusions and future work

In terms of the "proof-of-concept" intrinsically IL FLP, all of the experiments are completed and we hope to have a publication ready by the end of September. I am currently writing the publication and finalising what data will go into the publication. It is the aim that once this work is done, we can probe the system for fluorescent activity (briefly) and hence move our entire attention on to the deuteration reactions of the N-methyl acridinium bistrifylimide/lutidine ionic liquid FLP, in preparation/anticipation of carrying out experiments at ISIS at the end of September/ early October. Additionally, I will start to prepare my aural presentation for the Gordon Research Seminar, in which I was invited to speak at in August and my poster presentation for the associated GRC meeting.

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4. C. Hardacre, J. D. Holbrey, C. L. Mullan, M. Nieuwenhuyzen, W. M. Reichert, K. R. Seddon and S. J. Teat, *New J. Chem.,* 2008, 1953-1967.

QUILL Quarterly Report

May – July 2024

Name:	Sanskrita Madhukailya		
Supervisor(s):	Prof John Holbrey & Dr Leila Moura		
Position:	Final year PhD student		
Start date:	April 2021	**Anticipated end date:**	October 2024
Funding body:	TU-QUB Collaborative research degree		

Designing New LCST Ionic Liquids

This report mainly *outlines* the proposed structure of thesis (Intended title: Designing new LCST ionic liquids), planned to be submitted by October 2024. As is shown below, the objective and the outcomes of this research work, discussed in the previous quarterly reports, would be explained under 5 chapters.

Chapter 1 will concentrate mostly on the background and literature review, however, the subsections that are mentioned here, are subjected to change, depending on the conclusive storyline of the work and hence will be attempted at the very end. An exhaustive description on the history of lower critical solubility temperature phase behaviour, incorporating all the aspects like its importance, understanding, and applications in ionic liquid-water systems will be focused.

Chapter 2 will deal with the synthesis and characterisation of the ionic liquids that were studied throughout this work. A total of 28 ionic liquids, based on both monocationic as well as dicationic 5-phenyltetrazolate anions will be analysed depending on variations in their structures, that influences their behaviour with water. A detailed structure-property relationship study will be described, where variations in their thermo-physical properties, with respect to their structural modifications will be implemented. The experimental work from this chapter has been completed, with a few repetitive measurements on viscosity, density and DSC are yet to be carried out. Experimental work for the complete chapter should be ready by the end of July'24. A section each from this chapter and chapter 3 is in preparation for a publication, submitted to Prof. John Holbrey, for corrections.

Chapter 3 will include the extensive study made on the phase behaviours of the ionic liquids synthesised, when added to water. A detailed description in terms of full phase diagrams, spectroscopic, and crystallographic studies will be included to compare and contrast the various factors to consider while designing functional ionic liquids displaying LCST phase behaviours and how it can be controlled effectively, to be able to suit various applications like energy-efficient forward osmosis (FO) water desalination systems. This application-based study, focusing on a lab-scale FO process. is led by another PhD student and a co-author publication is also under progress. The experimental work from this chapter has also been completed, with some experiments are yet to be carried out for reproducibility and robustness. Experimental work for the complete chapter should be ready by the end of July'24.

Chapter 4 will deal with understanding the mechanism of LCST ionic liquid-water systems from their hydration and ion-associations through their liquid-structure studies from neutron scattering experiments. A section of this chapter will also include quantitative explanation of this phase behaviour from the energies of hydration/solvation carried out for a LCST and a non-LCST system, through isothermal titration calorimetric experiments. The neutron scattering experiments involves the synthesis of deuterated/perdeuterated ionic liquid, which has been tried in a small scale in the laboratory, however gram scale synthesis has been carried out in the D-lab at ISIS, Harwell campus at Didcot. A part of the experiment has already been carried out last year and the final few experiments are planned to be conducted in July’24 by Prof. John Holbrey at ISIS, before putting forward an explanation for a thesis chapter/publication. Simultaneously, ITC experiments on IL-water systems were carried out at ENS de Lyon under Prof. Margarida Costa Gomes and are awaiting for the treated results to be included into the chapter. Depending on the quality of results, another publication is expected to be prepared from this chapter in due course.

Chapter 5 will include the general summary and conclusion from this thesis work.

Chapter 6 will contain all the spectroscopic data, crystallographic tables, phase diagrams, TGAs, DSCs

QUILL Quarterly Report

May – July 2024

Name:	David McAreavey		
Supervisor(s):	Dr Stephen Glover, Dr Oana Istrate & Prof Peter Nockemann		
Position:	PhD Student		
Start date:	1st October 2021	**Anticipated end date:**	31st March 2025
Funding body:	Department for the Economy		

Design and Development of an Effective and Interconnected Smart Fire Suppression System for Lithium-ion Batteries in Electric Vehicles

Background

As many countries around the world begin to implement their plans to ban the sale of new petrol and diesel vehicles in the coming decades, there is a clear shift occurring towards electrification of transportation. However, there are several challenges that should be addressed if mass adoption of these vehicles is to be successful. Chiefly among which are the needs to extend range and improve battery safety. Depending on the sources used it can be argued that EVs do have a good battery safety record and the number of electric vehicle fires that occur are relatively low. Tesla's 2020 vehicle safety report claims that one of their vehicles is almost ten times less likely to be involved in a vehicle fire, than the average vehicle on the road in America per mile driven, based on data from the national Fire Protection Association and US Department of Transportation. Contrary to this, in London in 2019 based on data from the London Fire Brigade the incident rate when adjusted for the number of EVs and IC vehicles on the road is more than twice as high for EVs. Regardless of the exact frequency, when these cells are provoked it can often initiate thermal runaway, meaning that it is extremely difficult to extinguish as well as having the potential to burn both hotter and longer than a typical IC vehicle fire. The primary concern is of course for the safety of the occupants of the vehicle and the potential danger to their health. Additionally, an EV has the potential to ignite in scenarios where it may initially go unnoticed, usually if an IC vehicle ignites it will do so in use as this is when the highest temperatures are experienced. EVs on the other hand can ignite under a wider range of circumstances such as when charging. This means that the thermal runaway process may go unnoticed for some time as well as likely being close to a home or garage, causing significant property damage.

An additional concern surrounding the adoption of EVs is the level of media attention that EV fires receive. Despite being relatively infrequent especially due to the low total market share, the negative publicity generated hinders the adoption of these vehicles. As well as causing the loss of resources that were originally carbon intensive to produce.

Objective of this work

The ultimate goal is to develop a fire suppression and thermal management system that can be realistically employed in a vehicle. This work may only achieve a step in this development for such a suppression system. It is vital to consider that such a system must be compatible with thermal management systems, as the implementation of a fire suppression system without an appropriate thermal management system essentially renders the vehicle useless. This means that a vehicle has the ability to keep the cells within its pack in the optimal temperature range, promoting longevity. As well as having a sufficient suppression system that is capable of preventing the propagation of thermal runaway between cells in the event of a fault or road traffic collision.

Progress to date

Following on from last quarter this project is dependent on the successful COMSOL modelling of these runaway events. As such significant time has been invested in refining the 3D model. Despite this there are still some difficulties that have given cause to return to 2D simulations. These are generally significantly more stable and run in a much reduced time frame. Therefore, the plan at this stage is to survey a wide range of array designs in 2D before the refined area of interest is further investigated in 3D.

Alongside this modelling work strides have been made in developing a cell analogue that will complement the simulations. At this stage the first several prototypes of the cell analogue have been assembled and the first round of testing on the thermal properties have been undertaken.

Conclusions and future work

The development of the COMSOL model and rig remain the focus of the project. The final tests of the cell analogue need to be completed and a lager quantity of cell analogues produced.

QUILL Quarterly Report

May-July 2024

Name:	Emma McCrea		
Supervisor(s):	Prof Małgorzata Swadzba-Kwasny & Prof John Holbrey		
Position:	PhD student		
Start date:	01/09/21	**Anticipated end date:**	30/06/25
Funding body:	Engineering and Physical Sciences Research Council (EPSRC)		

Valorisation of Waste Polyolefin Plastics Using Lewis Acidic Ionic Liquids

Background

The deployment of innovative technologies is essential in addressing the environmental challenges posed by plastic waste, particularly in the case of polyethylene terephthalate (PET). One promising avenue is the utilisation of ionic liquids in the depolymerisation process, transforming PET into its monomeric building block, dimethyl terephthalate (DMT). This approach not only underscores the urgency of finding sustainable solutions for plastic recycling but also highlights the transformative potential of ionic liquids in advancing the circular economy.

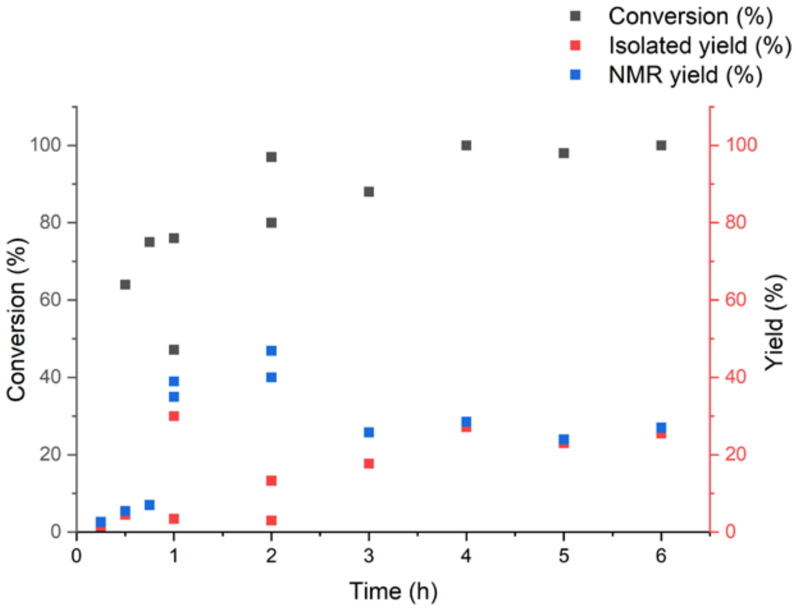
Ionic liquids, with their unique properties such as low volatility and tuneable chemical structures have emerged as versatile and efficient catalyst in various chemical processes. In the context of PET depolymerisation, the ionic liquids serve as catalysts, facilitating the breakdown of PET into DMT and paving the way for a more sustainable and resource-efficient plastic life cycle.

Objective of this work

The aims of this study are to first, investigate the efficiency of utilising ionic liquids as catalysts in the depolymerisation of polyethylene terephthalate (PET) to produce dimethyl terephthalate (DMT); and second, to assess the environmental and economic feasibility of incorporating ionic liquid-based depolymerisation into industrial scale recycling. Through a systematic exploration of reaction parameters, such as temperature, pressure, and ionic liquid composition, we aim to optimize the depolymerisation efficiency, maximizing DMT yield and selectivity while minimizing energy consumption.

Progress to date

Initial experiments with PET at 100°C indicated that higher temperatures and increased catalytic loading are necessary. The reactions were conducted using two different methods: ionic liquid as the solvent and methanol as the solvent, resulting in distinct outcomes. It was discovered that water cannot be used in the separation process to remove the product, as it hydrolyses the product into unwanted terephthalic acid (TPA). Instead, hot and cold methanol were employed to recrystallise and separate the unreacted PET and ionic liquid from the product. When using the ionic liquid as the solvent, it was challenging to obtain a pure product from the reaction mixture, which negatively affected the yield. Conversely, using methanol as both the solvent and the reactant facilitated the separation and isolation of the product, as it precipitated out of the reaction mixture upon cooling.



Conclusions and future work

Continuation of reaction condition optimisation and kinetic study with analysis by NMR, TGA, DSC, and FTIR. Future work will include a study on the reusability of ionic liquids.

QUILL Quarterly Report

May 2024 – July 2024

Name:	Kerri McKeever		
Supervisor(s):	Prof Gosia Swadzba-Kwasny & Prof John Holbrey		
Position:	PhD Student		
Start date:	14/08/2023	**Anticipated end date:**	13/08/2026
Funding body:	DfE CAST, Diamond and ISIS		

Boron and Frustrated Lewis Pairs in Supported Ionic Liquid Phases: An Interdisciplinary Study of New Metal-Free Catalysts

Background

An emerging alternative for transition metal catalysis is using Lewis acidic boranes in Frustrated Lewis pairs. Frustrated Lewis pairs (FLPs) are compounds which contain a Lewis acid and base (eg. boron/phosphine) that are either electronically or sterically hindered, preventing formation of the classical adduct, instead, in solvent they form an encounter complex in which the acid and base remain weakly associated, with the HOMO of the base and LUMO of the acid left free for reactivity with a third molecule. This unique behaviour allows for the activation of H_2 and other small molecules (eg. CO2, N2), meaning they are capable of conducting metal-free catalysis and a possible alternative to transition metals.

Analytical techniques involving X-rays and neutron scattering, including operando studies are well established for transition metal catalysis, however, the same cannot be said for boron compounds, which face a number of different challenges for example: boron is a light element and its K-edge is in the soft X-ray regime, thus for XAS studies, a vacuum is required, yet for FLP hydrogenation reactions a H_2 atmosphere is needed preventing investigation by standard methods. In this project, this will be mitigated by using ionic liquids which have a negligible vapor pressure and can be studied under high vacuum. Another challenge is the bubbling of gas through a liquid in operando studies, to overcome this we will be using supported ionic liquid phases (SILPs), where the film of an ionic liquid is supported on a porous solid. X-ray Raman spectroscopy will also be used to study boron- based FLPs, a new hard x-ray technique that can study the bulk structure of low Z materials. For neutron scattering, ^{10}B (ca 19% of natural B) absorbs neutrons well and provides poor scattering data, so isotopically pure boron compounds will be used. Additionally, DISSOLVE, a new alternative to EPSR will be used to model the experimental data.

Objective of this work

This project aims to expand the understanding and knowledge of FLP chemistry to hopefully be a viable alternative to transition metal catalysts and develop analytical techniques such as x-rays and neutron scattering to study light elements, specifically boron and overcome the challenges which accompany that. Additionally, to expand the knowledge and expertise of XRS at Diamond and in the UK, as it becomes an increasingly popular technique.

Progress to date

During May I continued the synthesis of BcatBu. This synthesis was tricky, we tried a few different methods, but I eventually was apply to successfully make this compound. This is a boron compound which we previously measured using XRS but not using soft XAS, along with $B(Ph)_3$, so during this month I also applied for Rapid Access at B07 at Diamond Light Source for these two compounds, this proposal got approved and I sent the compounds off for analysis.

I also attended Diamond Light Source for a data analysis workshop, which informed me of how to use different data processing and modelling software for X-ray data, it was heavily informative, and I shall be making use of these software throughout the course of my PhD.

Throughout this quarter, I also attended a Spectroscopy User Meeting at Diamond Light Source, where I presented a poster on my work, this meeting displayed people from different fields which have used x-rays in their work, it was very informative and gave me the opportunity to meet more people in the field.

Additionally, I attended the ISIS Deuteration Meeting which was very useful in that I met many people in the deuteration community and discussed problems and ideas for the ISIS deuteration group.

I continued with my XRS data analysis, I completed the background subtraction and fitted them to a Gaussian graph to get the peak area, to be able to compare this between different B K edge and draw conclusions on the Lewis acidity.

I also was able to train some interns on how to use the glovebox, I myself was trained to use the TGA and I helped to clear out the chemicals in the QUILL chemical store.

In June, I had my Differentiation, the review towards the end of the first year of your PhD, it went successfully, I passed with some recommendations of what to include in the future and how to move forward with my project.

In July, I attended the EuChemS Conference in Dublin for 4 days. I presented a poster and attended talks on a wide variety of different chemistry topics including group 13 metal reactions to the story of the first woman to gain a PhD in chemistry.

Additionally, I spent my time synthesizing $Na[^{11}B(pyrazole)_4]$ for a beamtime at ISIS oon the SANDALS instrument. The synthesis was tricky it involved multiple steps but I was able to complete it. I then attened the beamtime at ISIS Neutron and Muon Source.

Conclusions and future work

During this quarter I attended multiple meetings, workshops and conferences at Diamond, ISIS and in Dublin where I presented a poster on my work, I also completed my Differentiation, while continuing to work on the XRS data, and attending a beamtime at ISIS.

Going forward, I will be preparing for the upcoming QUILL meeting, preparing samples and completed the deuteration of these samples for two upcoming ISIS experiments in September and an additional beamtime in January, whilst continuing to understand the XRS and XAS data.

QUILL Quarterly Report

May – July 2024

Name:	Shannon McLaughlin		
Supervisor(s):	Professor Gosia Swadźba-Kwaśny		
Position:	PhD Student (4th year)		
Start date:	October 2020	**Anticipated end date:**	October 2024
Funding body:	Department for the Economy (DoE)		

Ionic Liquids Based on Silicon Cations

List of Chapters:

Chapter 1: Phosphonium ionic liquids

This chapter will introduce the properties, industrial applications and synthesis of phosphonium ionic liquids. It will also introduce the concept of liquid-liquid transitions (LLT) and discuss the motivation to design ionic liquids with potential for LLT. The experimental section will include synthetic procedures and characterisation for various $[P_{666,14}]$+ ILs. The results and discussion section will explore challenges faced when synthesising specific phosphonium ILs and summarise the main outcomes of the collaboration with the Wojnarowska group.

Chapter 2: Frustrated Lewis pairs in ionic liquids

This chapter will consist of an introduction to frustrated Lewis pairs in ionic liquids, the mechanism of FLP activity and experimental evidence of the encounter complex. The experimental section will include the synthesis, purification and characterisation of various bistriflimide ionic liquids as well as the preparation of FLP/IL solutions. It will also discuss hydrogen bubbling experiments and GC studies.

Chapter 3: Silylium ionic liquids

This chapter will consist of an introduction to silylium cation chemistry. The experimental section will include synthetic procedures for generating $[Si(Mes)_3]^+$ containing compounds as well as complete characterisation studies.

Expected submission date: 31st October 2024

QUILL Quarterly Report

May – July 2024

Name:	Beth Murray		
Supervisor(s):	Prof Małgorzata Swadźba-Kwaśny & Prof John Holbrey		
Position:	PhD		
Start date:	October 2022	**Anticipated end date:**	January 2026
Funding body:	Department of Economy		

Inorganic Chemistry of Group 13 Elements in Sustainable Uses

Background

In the last quarter, I have been extending the research I carried out at Monash University in Melbourne, looking into liquid coordination complexes (LCCs) as electrolytes for aluminium batteries.

Regarding electrolytes for aluminium batteries, rechargeable batteries hold a crucial position in the energy management strategy of the European Union (EU). The EU acknowledges energy storage solutions as essential elements that contribute to grid flexibility and support the seamless integration of renewable energy sources into the energy system.[1] Secondary (rechargeable) batteries exhibit exceptional energy conversion efficiency, superior performance, reliability, and the ability to provide on-demand responses.[2] Presently, lithium-ion batteries are considered cutting-edge technology, however, they are plagued by high costs and flammability concerns. These batteries are widely prevalent in mobile electronic devices and are being increasingly utilized in transportation and grid applications.[1] Lithium-ion batteries offer several advantages, including high energy density, design flexibility, self-discharge, good cycle life, and low maintenance.[3] However, it is important to note that lithium has a low abundancy on Earth, which contributes to its high cost and reduces the long-term sustainability of relying heavily on the metal. Furthermore, as already mentioned elemental lithium is unstable and highly flammable.[4]

Metals from Groups 1 and 2 have been considered as substitutes for lithium (Li) in batteries, but aluminium (Al) from Group 13 appears to hold significant promise. It is abundantly available on Earth, making it a cost-effective option. Moreover, aluminium offers safe handling, the capability to exchange three redox electrons per cation, and exhibits high gravimetric and volumetric capacity.[5] One drawback of Al batteries is their limited commercialisation, primarily due to the absence of suitable electrolytes. Many attempts to commercialise Al batteries faced technical challenges, including difficulties in achieving reversible electroplating/stripping of aluminium, inadequate stability of Al-ion cells, and corrosion issues.[1] While there has been significant research on electrolytes for lithium-ion batteries, limited attention has been given to finding suitable electrolytes for Al batteries. However, ionic liquids (ILs) have emerged as a promising candidate. ILs are composed entirely of ions and often have a melting point below ambient temperature. They possess several desirable properties, including high ionic conductivity, minimal volatility, very low flammability, and excellent chemical and electrochemical stability.[3] Promising electrolytes were developed through the dissolution of aluminium salts, such as $AlCl_3$ or $Al(TFSI)_3$, in ionic liquids containing bis(trifluoromethanesulfonyl)imide ($[TFSI]^-$) or trifluoromethanesulfonate ($[OTf]^-$) anions.[6, 7] While electrolytes using ILs show promise, they also present certain challenges, such as cost. Despite the cost advantage of aluminium over lithium, the use of ionic liquids can introduce additional expenses. The organic cation, despite having a spectator role, contributes significantly to the overall cost. Secondly, one of the challenges associated with using ILs is their higher viscosity compared to organic solvents, which hampers the conductivity of Al(III). Another significant drawback is corrosion, especially in chloride-containing systems, which remains a critical issue. Lastly, there is a limited scope for optimisation when using ILs as electrolytes. The concentration of Al(III) is constrained by the solubility of the aluminium salt, and also by the potential negative effects that high salt concentration can have on the electrolyte, such as an increase in viscosity that can be detrimental to conductivity.

At this juncture, we introduce LCCs as novel analogues of ILs that have been developed specifically to address the challenges encountered with ILs in various applications. LCCs supply the demand for cost-effective analogues of ionic liquids that possess, high metal content, and adjustable environments around the metal centre. These analogues are highly sought after for applications such as metal electrodeposition,[8] Lewis acid catalysis,[9] and as electrolytes for lithium-ion batteries.[10]

Objective of this work

The primary goal of the research on liquid coordination complexes (LCCs) for aluminium battery electrolytes was initially centred around synthesising semiconductor nanoparticles through the utilisation of LCCs. This segment of work work concentrates on the use of liquid coordination complexes based on aluminium as electrolytes in aluminium-ion batteries. This research is founded on the promising potential of aluminium in batteries, attributed to its high abundance on Earth, its capability to exchange three redox electrons per cation, as well as high gravimetric and volumetric capacity.[5]

Progress to date

Regarding previous quarterly reports, work had been carried out at Monash University in Melbourne, Australia for six weeks, as part of the Macfarlane research group. In the initial stage of the research, the objective was to reproduce the literature data on the utilization of a urea-$AlCl_3$ LCC as an electrolyte in aluminium batteries. The LCC electrolyte had received considerable attention in previous publications, making it a suitable candidate for replication using a coin cell configuration. Coin cells were selected for this study due to their ability to operate with minimal electrolyte, allowing for symmetrical and full cell experiments to be conducted, although no literature had reported the use of a coin cell. Figure 1 shows the preliminary results obtained from galvanostatic cycling test performed on symmetrical Al/Al cells, employing the urea-$AlCl_3$ electrolyte ($\chi_{AlCl_3} = 0.58$). Unfortunately, initial findings showed a high overpotential of approximately 2 V, and cell shorting, which from further investigation proved to be that the Al discs needed to be polished before use, likely due to the presence of a residual oxide layer on the surface.[11]

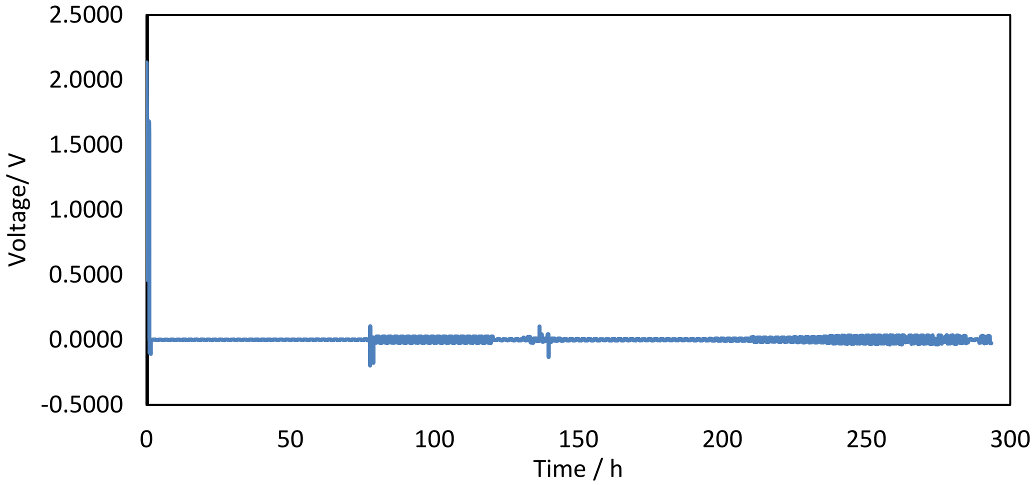


Figure 1 - Galvanostatic cycling of Al/Al symmetrical cell with urea-$AlCl_3$ electrolyte.

A polishing solution was prepared by combining sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4) and nitric acid (HNO_3) (further details in section 5.2.2). After polishing of the Al discs, the cycling results were comparable to literature,[5] showing a lower overpotential and stable cycling (Figure 2).

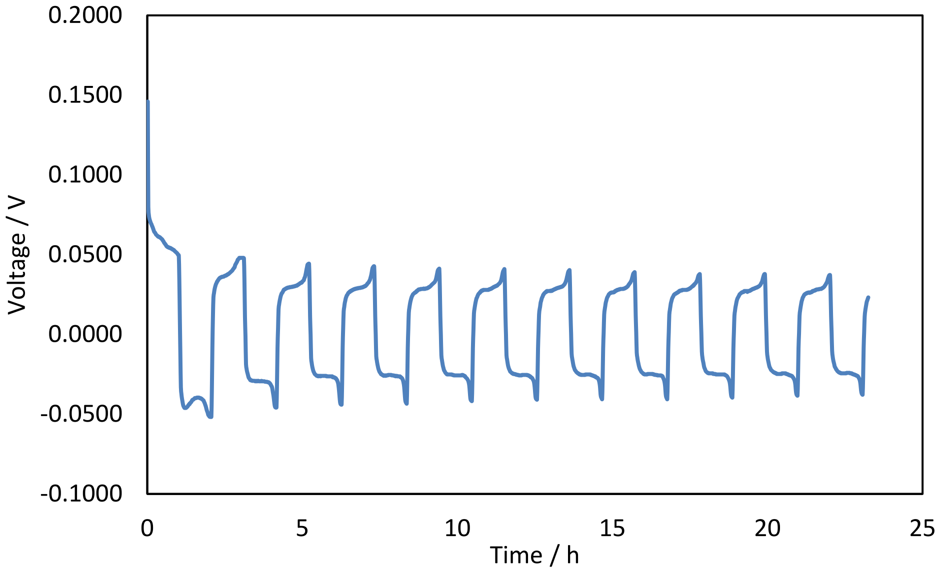


Figure 2 - Galvanostatic cycling of Al/Al symmetrical cell with urea-$AlCl_3$ electrolyte, after the Al electrodes were polished with acid.

EMImCl-$AlCl_3$, a non-flammable IL that operates at room temperature, has gained significant attention as a favoured electrolyte for aluminium batteries. This IL exhibits notable attributes, including high ionic conductivity, exceptional thermal stability, chemical stability, and electrochemical stability.[12] In 2016, Sun *et al.* conducted a study investigating the impact of incorporating various common solvents, such as acetone, acetonitrile, tetrahydrofuran (THF), toluene, and dichloromethane (DCM), into the EMImCl-$AlCl_3$ IL. Cyclic voltammetry (CV) was employed as a screening method to assess the impact of solvents on the electrochemical activity of the solution. This technique was utilized to determine whether the interaction between the IL and a solvent induces significant changes in the electrochemical behaviour. interestingly, certain solvents like tetrahydrofuran (THF) and acetonitrile were found to negatively affect the performance of the electrolyte. In contrast, the addition of DCM and toluene not only sustained the deposition and stripping of aluminium effectively but also resulted in a notable improvement in current density. Specifically, the current density was enhanced by 13% with the addition of toluene and 10% with the addition of DCM, surpassing the performance achieved with the pure IL.[13] The urea-AlCl$_3$ is known to be a less effective electrolyte than EMImCl-AlCl$_3$, due to its higher viscosity and lower ionic conductivity.[14] In an attempt to explore similar effects observed in the EMImCl-AlCl3 system, we opted to incorporate DCM and toluene into the urea-AlCl3 LCC, to assess if such addition could enhance the performance of the electrolyte in any manner. Unfortunately results showed an equimolar blend of urea-AlCl3 and DCM led to a substantial increase in overpotential compared to the LCC electrolyte without DCM (Figure 3).

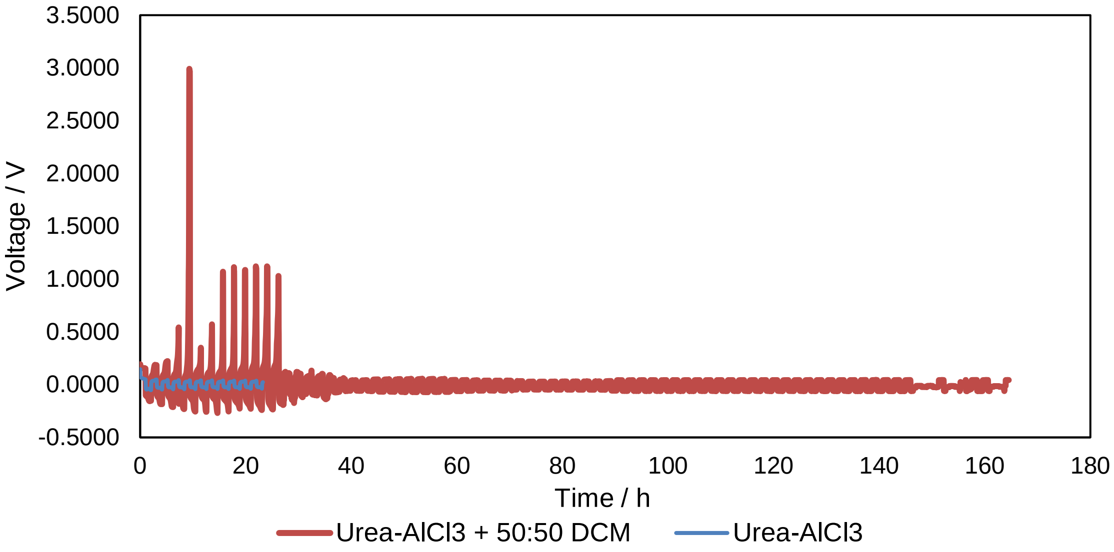


Figure 3 - Comparison of symmetrical Al/Al cycling with urea-AlCl$_3$ electrolyte and urea-AlCl$_3$ electrolyte with the addition of equimolar amounts of DCM

The urea-AlCl$_3$ electrolyte was also studied with the addition of toluene (50% w/w) to explore the possibility of further enhancing the system. Symmetrical Al/Al cycling demonstrates promising outcomes, with the electrolyte performing well, particularly at higher current rates (Figure 4). This is a promising outcome, as to date no literature has reported on a urea-AlCl$_3$ electrolyte with the addition of toluene. As previously mentioned, a drawback of urea-AlCl$_3$ as an electrolyte, is its lower conductivity (≈ 5 mS/cm) than the ionic liquid electrolyte EMImCl-AlCl$_3$ (≈ 20 mS/cm). The conductivity of the LCC with the addition of toluene 50% w/w was investigated and showed to be around 4 mS/cm better than the LCC without toluene (≈ 9 mS/cm) (Figure 5).[15] While this initial progress is encouraging, further investigations are required to assess whether this system is a viable option for Al-ion batteries. These upcoming studies will encompass physical characterisations like viscosity, but the focus will primarily be on ionic conductivity. Additionally, I intend to experiment with different w/w% of toluene added to determine the optimal conditions.

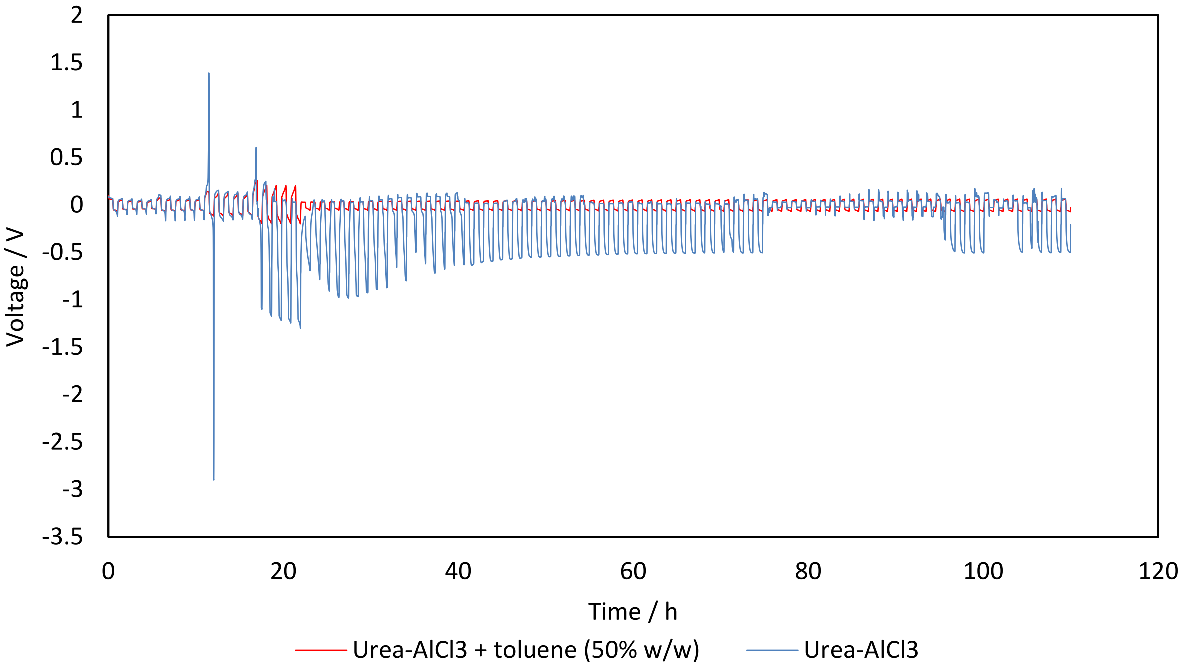


Figure 4 - Comparison of symmetrical Al/Al cycling with urea-$AlCl_3$ electrolyte and urea-$AlCl_3$ with the addition of toluene (50% w/w).

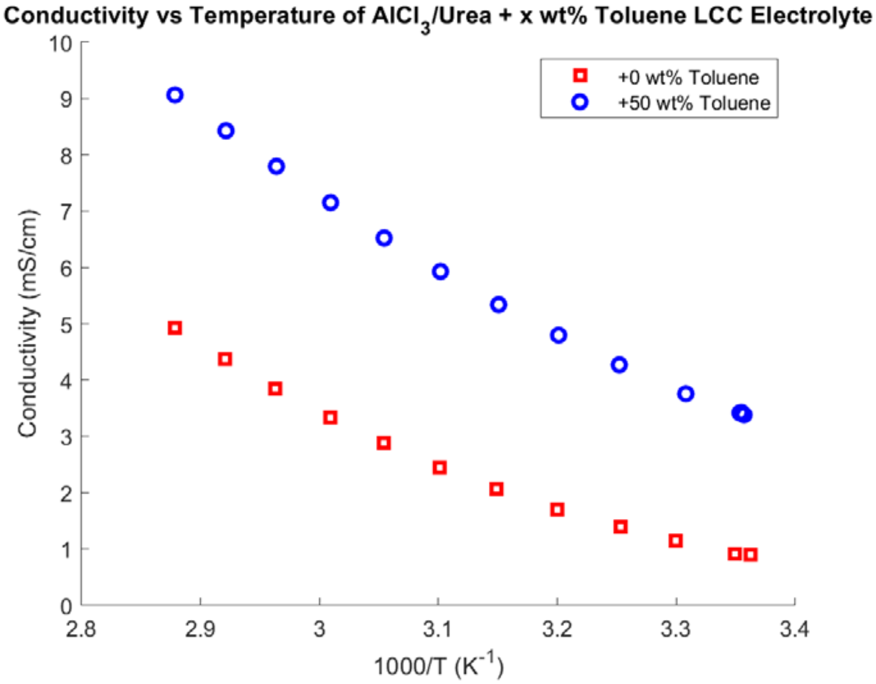
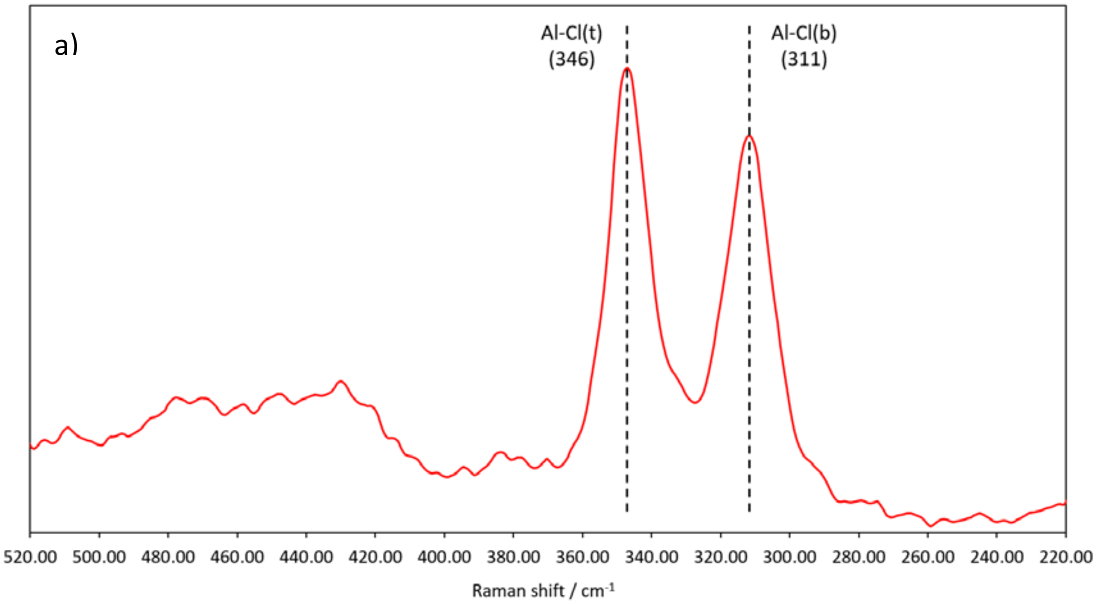


Figure 5 - Conductivity of urea-$AlCl_3$ + wt% toluene.

As mentioned earlier, a coin cell configuration was utilised for all the studies due to the restricted supply of materials needed for preparing the electrolyte. This setup proved to be satisfactory for the Al/Al symmetrical cycling experiments. However, challenges arose when transitioning to a full cell configuration. A full cell configuration was made using a graphite cathode. The cyclic voltammetry (CV) results from the urea-$AlCl_3$ cell showed a trace similar to that reported in literature,[16] however, with an additional oxidation peak around 1.3 V (Figure?). To identify the nature of the additional peak, several coin cells with different independent variables were tested. One of these coin cells ran without a graphite electrode but only the carbon fiber paper support, and the peak was still observed. This result indicates that the graphite electrode was not the cause of this side reaction. Next, a coin cell experiment was conducted without the entire graphite cathode and support. In this test, the electrolyte was in direct contact with the stainless steel coin cell. Surprisingly, the oxidation peak remained present, implying that a side reaction might be occurring between the urea-AlCl3 electrolyte and the stainless steel coin cell. To conclusively confirm our speculation, a final test was conducted using a coin cell with an aluminium triflate ($Al(OTf)_3$) in diglyme electrolyte. This test showed no oxidation peak at 1.3 V, providing further evidence that the reaction occurs between the urea-AlCl3 electrolyte and the stainless steel coin cell. This is likely attributed to corrosion issues associated with chloride electrolytes,[17] as it interacts with the coin cell.

To investigate the impact of toluene on the urea-$AlCl_3$ LCC, speciation studies, which include Raman and NMR were conducted on both the pure LCC, neat toluene and the LCC containing toluene. The Raman studies indicate that the peaks observed in the pure compounds are still present in the mixture, suggesting that the bonds in the pure compounds remain unaffected when the two are combined (Figure 6).



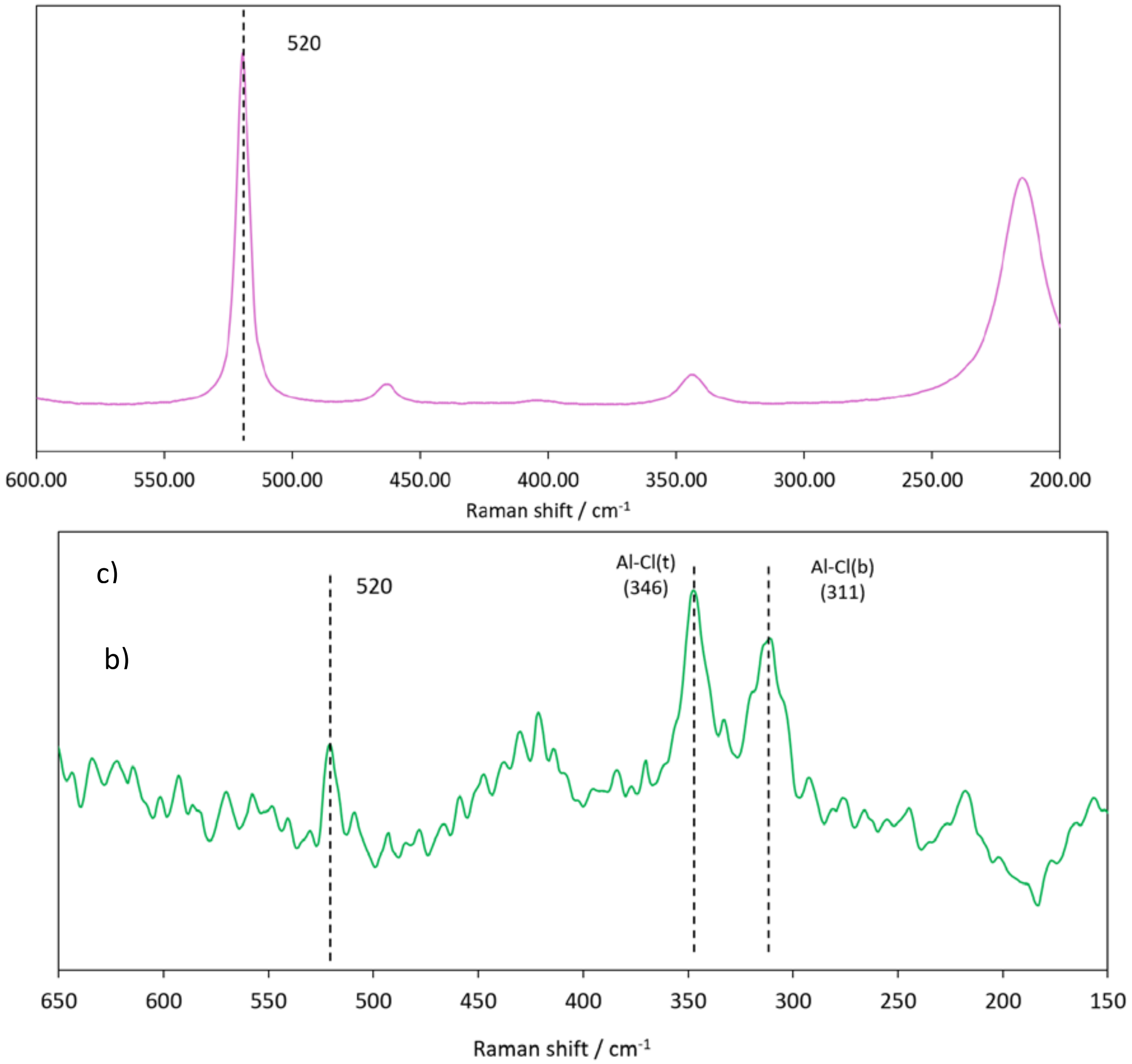


Figure 6 - Raman spectra of a) pure LCC, b) pure toluene and c) LCC + 25% toluene

Figure 7 shows the ^{1}H NMR spectra for urea-$AlCl_3$ with toluene (25%, 50% and 75%), neat urea-$AlCl_3$ and neat toluene. The neat toluene NMR has a cluster of peaks from 6.5-6.8 ppm, corresponding to the aromatic protons, and the singlet at 1.75 ppm corresponds to the three protons of the CH_3 group. It can be seen from the spectra that the CH_3 peak is still present when toluene is mixed with the LCC at all three ratios. This suggests that $AlCl_3$ didn't extract a proton from the CH_3 group to form a carbocation. All peaks shift more upfield, due to an increased electron density.

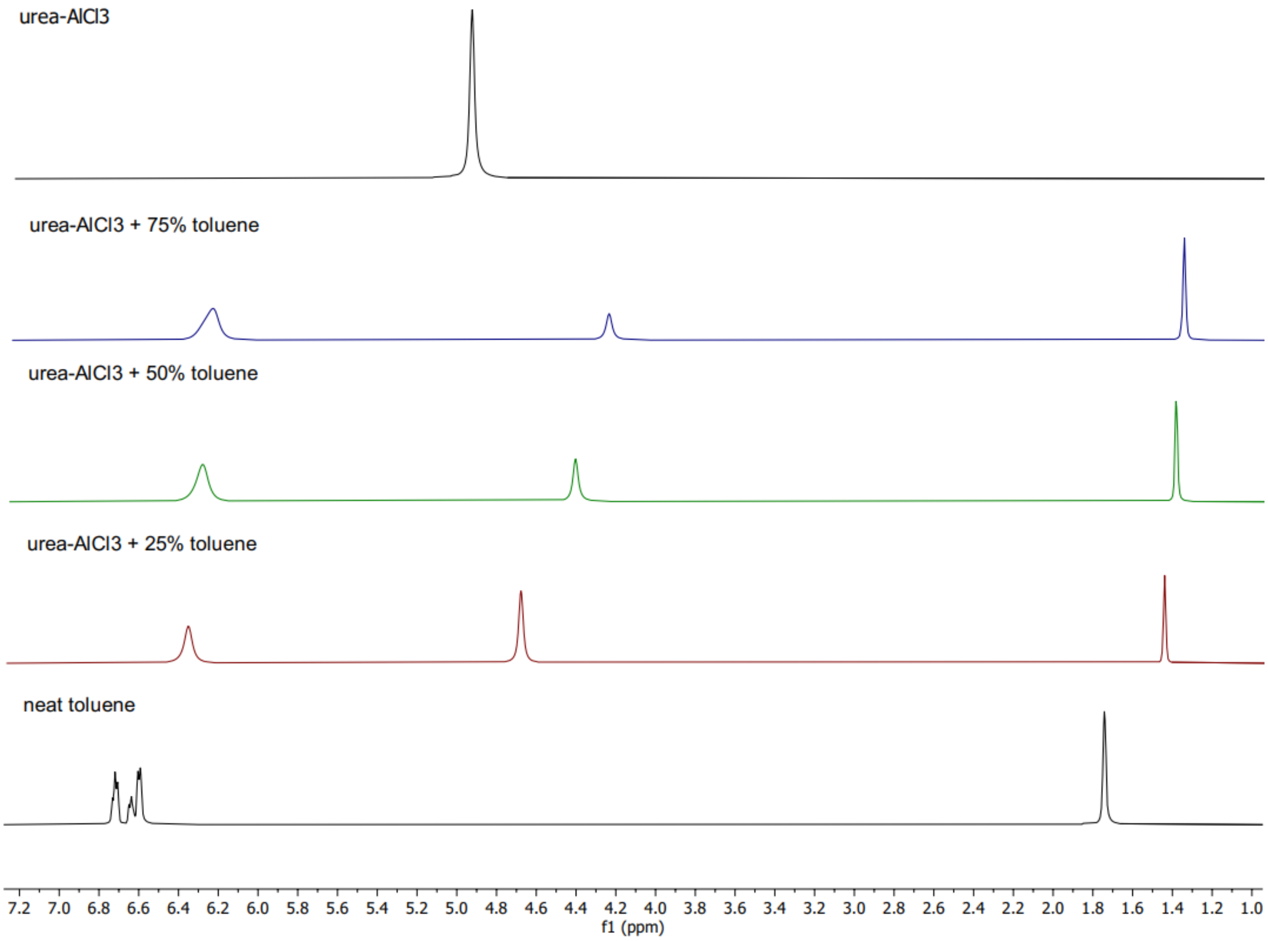


Figure 7 - ^{1}H NMR comparison of urea-$AlCl_3$ with toluene (25%, 50% and 75%) with neat urea-$AlCl_3$ and neat toluene. NMR solvent: d_6-DMSO (capillary).

Figure 8 shows the ^{13}C NMR NMR comparison of urea-$AlCl_3$ with toluene (25%, 50% and 75%) with neat urea-$AlCl_3$ and neat toluene. From the spectra it can be seen that all toluene peaks are present, therefore, the structure of toluene is unaltered when mixed with urea-$AlCl_3$. The one carbon peak of urea is also retained when mixed with toluene.

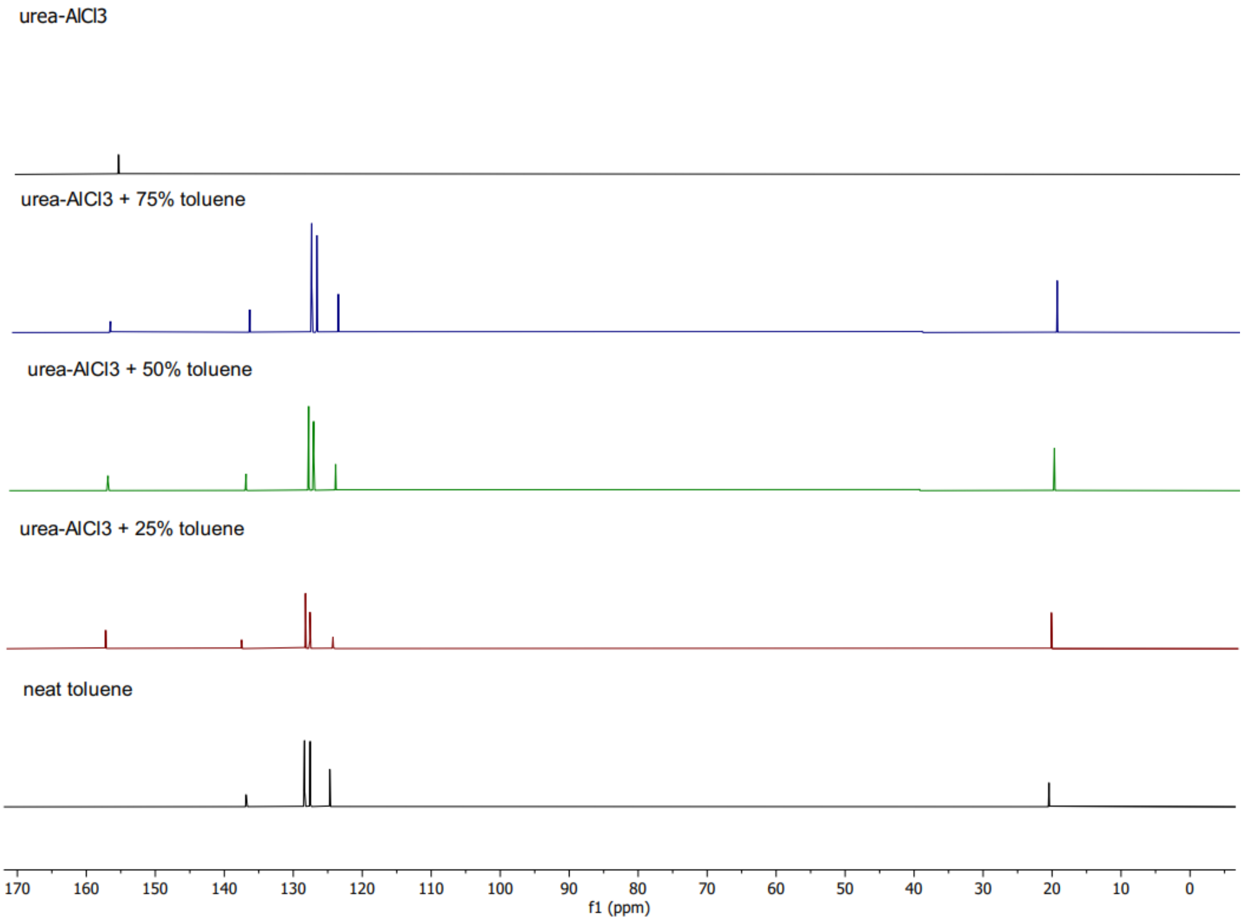


Figure 8 - ^{13}C NMR comparison of urea-AlCl$_3$ with toluene (25%, 50% and 75%) with neat urea-AlCl$_3$ and neat toluene. NMR solvent: d$_6$-DMSO (capillary).

In order to study the coordination environment of aluminium in the LCC when toluene was added, ^{27}Al NMR was carried out (Figure 9). The neat LCC has a broad peak around 77 ppm, but when toluene is added the peak shifts downfield to approximately 95 ppm. Due to the chemical shift, it can be deduced that the Al species with and without toluene are both four coordinate. This is because the peaks are in the region corresponding to four coordinate Al species. However, due to the change in chemical shift from 77 to 95 ppm, it can be assumed a different four-coordinate species is formed, although it is not yet clear what.

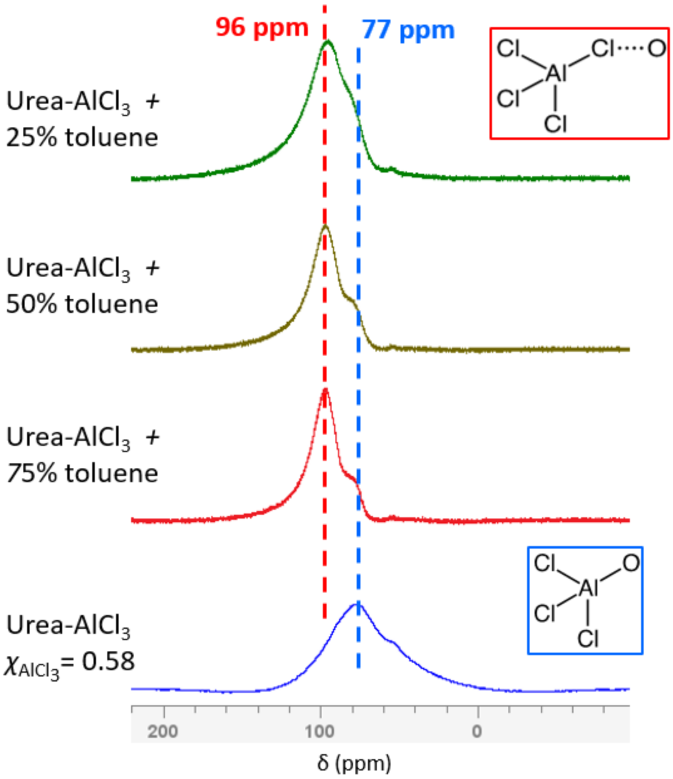


Figure 9 - ^{27}Al NMR comparison of urea-AlCl$_3$ with toluene (25%, 50% and 75%) with neat urea-AlCl$_3$ and neat toluene. NMR solvent: d$_6$-DMSO (capillary).

A quick experiment was also carried out comparing the mixing of the LCC with methylcyclohexane in comparison to toluene. The reason behind this study was to see if the interaction between toluene and urea-AlCl$_3$ is due to the μ-system present in toluene, as methylcyclohexane is a similar structure with the same number of carbons, but no double bonds present (Figure 10). In contrast to toluene, when methylcyclohexane is added to urea-AlCl$_3$ the resulting mixture is immiscible, clearing forming two layers (

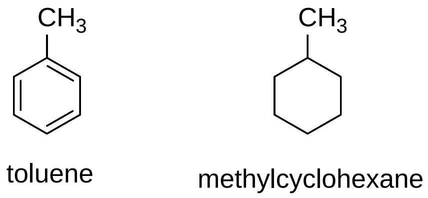


Figure 10 - Chemical structures of toluene and methylcyclohexane

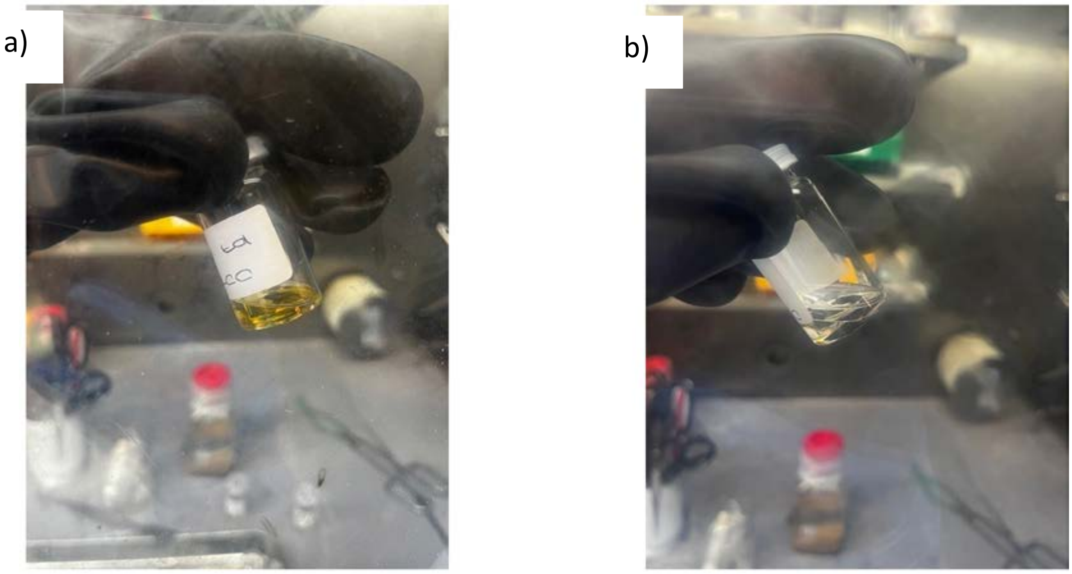


Figure 11 - a) toluene mixed with LCC to form one layer and b) methylcyclohexane mixed with LCC to form two layers

This suggests that the µ-bonds in toluene are interacting with the LCC, allowing for a homogeneous mixture to form.

Conclusions and future work

The literature findings on the use of urea-AlCl3 (χ_{AlCl_3} = 0.58) as an electrolyte for Al batteries were successfully reproduced using a coin cell configuration. Galvanostatic symmetrical cycling demonstrated stable performance once the aluminium electrodes were polished with an acid mixture to ensure the elimination of any residual oxide layer on their surfaces.
TOPO-$AlCl_3$ (χ_{AlCl_3} = 0.60) exhibited intriguing outcomes as an electrolyte, including high stability. However, its potential use as a battery electrolyte is likely hindered due to the size of the ligand, as it is not expected to function effectively as a charge carrier.

Continuing with the research on the urea-$AlCl_3$ electrolyte, additional investigations involved examining the impact of additives, such as DCM and toluene, on the electrolyte's performance. Unexpectedly, the addition of DCM had a detrimental effect on the galvanostatic symmetrical cycling, as results show high overpotentials. However, the addition of toluene yielded much more promising results, as the electrolyte performed well, showing good stability at much higher current rates.

This study has also revealed that coin cells are unsuitable for this research due to the corrosive nature of chloride electrolytes. The CV results indicated that an oxidation reaction was taking place between the urea-$AlCl_3$ electrolyte and the stainless steel of the coin cell, necessitating the search for an alternative cell option. Our collaborators at Monash University have undertaken efforts on an alternative cell, currently in the testing phase as a laminated pouch cell.

Brief speciation studies using Raman and NMR techniques have offered valuable insights into the impact of toluene on the urea-$AlCl_3$ LCC. This exploration aims to elucidate the reasons behind the improved performance of the electrolyte with the addition of toluene. A proposal for a neutron scattering experiment as ISIS has been submitted to gain a further understanding of the distribution of urea and toluene around aluminium, with beam time scheduled for the start of October.

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QUILL Quarterly Report

May 2024 – July 2024

Name:	Junzhe Quan		
Supervisor(s):	Prof John Holbrey & Dr Leila Moura		
Position:	PhD Student		
Start date:	01/10/2019	**Anticipated end date:**	15/04/2025
Funding body:	Self-funding		

Use Ionic Liquids that Exhibit LCST (Lower Critical Solution Temperature) Behaviour as Draw Fluids for Ewater Treatment, Desalination and Separation

List of Chapters:

Chapter 1: Literature Review

Chapter 2: Building a new method to measuring cloud points of ionic liquid (IL)-water system by using Crystal16

Chapter 3: Setting up the Lab-scale Forward Osmosis test system and benchmark

Chapter 4: Using lab-scale FO test machine to test tetrabutylphosphonium 5-phenyltetrazolate solution as draw solute both under FO and PRO modes

Chapter 5: COSMO-therm simulation and modeled economic cost in industry

Chapter 6: Conclusion and Future work

Expected Submission Date:
January 2025

QUILL Quarterly Report

May – July 2024

Name:	Michael Sweeney		
Supervisor(s):	Dr Leila Moura & Prof John Holbrey		
Position:	PhD Student		
Start date:	Oct 2023	**Anticipated end date:**	Oct 2026
Funding body:	CAST Award (DfE & Chevron)		

CO_2 Capture from Commercial Flue Gas Process Streams

Background

The removal of CO_2 from flue gas is crucial to curbing greenhouse gas emissions into the atmosphere. As the effects of climate change begin to set in across the global, governments across the world have come together and agreed to reduce emissions, setting themselves targets and new maximum emission limits.[1–4] Industry will need to optimise or develop technologies to prevent the atmospheric escape of CO_2 generated by industrial processes accounting for around 21% of emissions.[3] The current industrial standard using amine scrubbers is energy intensive and has other drawbacks regarding recycling and corrosion.[5] Our goal is to develop new processes that have potential industrial application and outperform the current industrial standard amine scrubbers.

There has been much research into the use of different amines and blending different amines together to mitigate some of these drawbacks.[6] Among some of the widely applied amines are monoethanolamide (MEA)[7] a primary amine, methyldiethanolamine (MDEA) a secondary amine and piperazine (PZ) a cyclic amine.[6] The structures are shown in Figure 1. While exact mixtures vary by company the amine that is applied the most often in blends MEA.[7] MEA has a high viscosity and the standard practice it to dilute it with water to 30 wt%.[8,9] This however has its own complications with water's high heat capacity requiring extra energy to reach desorption temperatures of 100-120 °C to release the CO_2.[9] Couple this with the mass loss at the operating temperatures, it's a system fit for redesign.

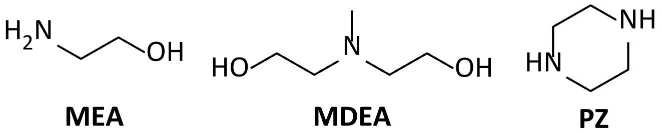

Figure 12 -Structure of common amines used in CO_2 scrubbing

Different attempts have been employed in reducing the amount of water with other solvents and added organic solvents to mitigate the shortcomings of the aqueous system. While this helped decrease the energy input viscosity problems persisted.[10]

There are other drawbacks such as degradation of the amine solution as the amine solution eventually breaks down to form corrosive byproducts, incurring additional cleaning costs. MEA is used as the industrial benchmark over other amines for its low cost and effectiveness.

MEA (**1**, Figure 2) captures CO_2 through chemisorption, it binds the CO_2 to form the carbamate (**2**, Figure 2) byproduct along with the pronated amine (**3**, Figure 2) which can regenerate CO_2 upon heating. Water can also capture CO_2 forming the bicarbonate (**4**, Figure 2) which is in equilibrium with the carbonate (**5**, Figure 2) species.

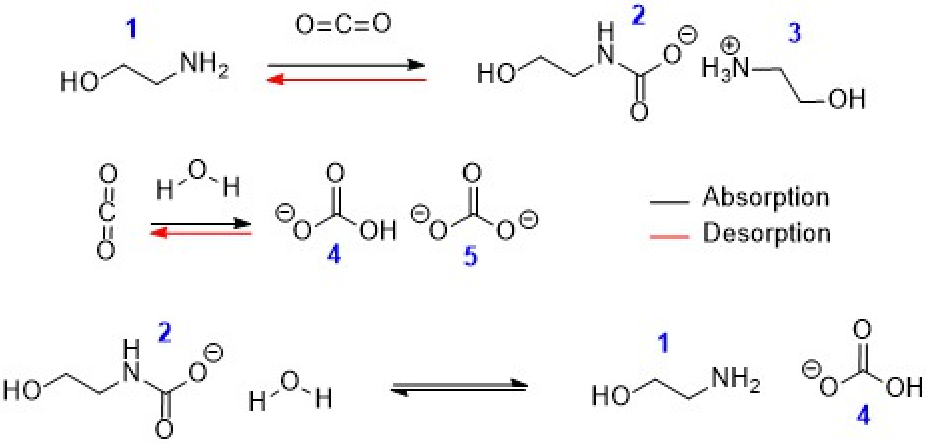

Figure 13 - Reaction pathway for MEA & CO_2

Due to issues with amine scrubbers outlined above a replacement is needed. One such potential replacement are protic ILs like 1,8-Diazabicyclo[5.4.0]undec-7-ene imidazolide [DBUH][Im] and 1,8-Diazabicyclo[5.4.0]undec-7-ene 1,2,4-triazole [DBUH][Triz] that are synthesised through an acid-base neutralisation reaction due to their easy synthesis and their relative commercial competitivity with amines. (structure shown in Figure 3). Protic ILs also have the potential for high thermal stability and can be functionalised towards enhanced CO_2 capture. There is also the potential for lower energy input for desorption than the 30 wt% MEA solution.

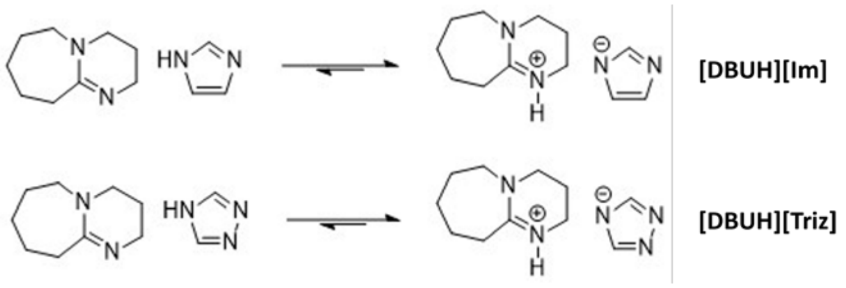

Figure 14 - Synthesis of protic ILs

Objective of this work

The main objective of this project is to design a solvent that can capture CO_2 from commercial process flue gas streams. That can effectively remove CO_2 at low partial pressure (40 mbar) and high temperatures (90-160 °C) i.e. industrial conditions. One such solvent which is under investigation is protic ILs.

Progress to date

The thermal stability of the ILs are important due to the recyclable nature of the absorption/desorption process for CO_2 capture which happens at high temperatures (90-160 °C) for industrial scrubbing.

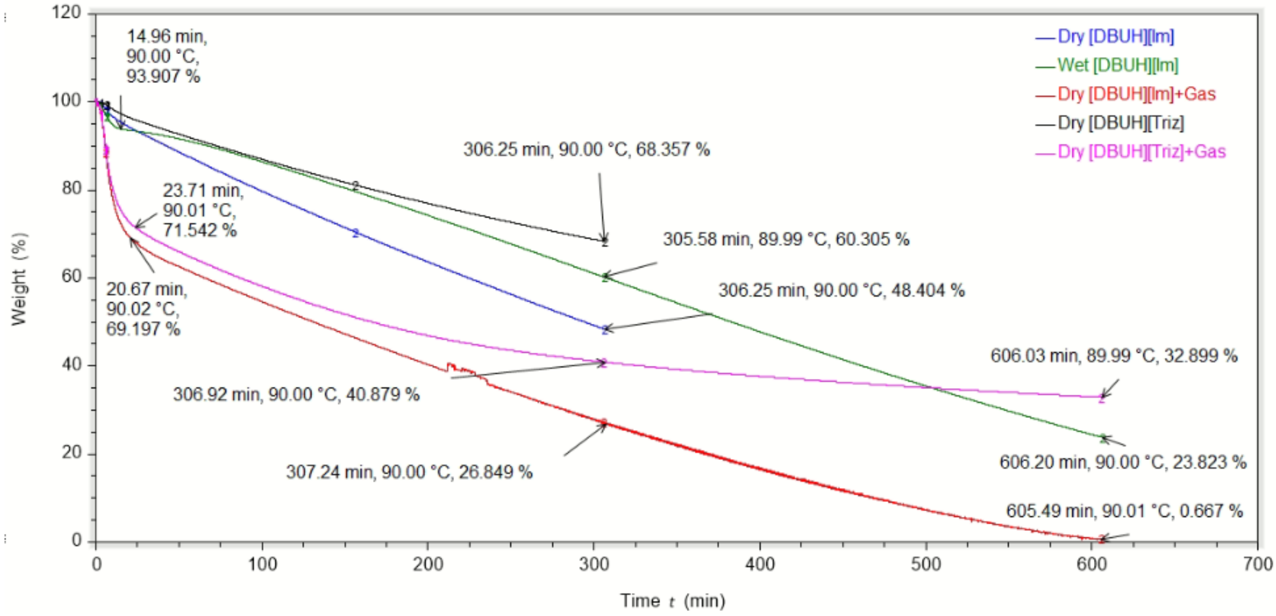

Figure 4 - 90 °C isothermal TGA. Gas = CO_2. Blue line; dry [DBUH][Im] (>0.1 wt% water). Green line; wet [DBUH][Im] (14 wt% water). Red line; dry [DBUH][Im] (>0.1 wt% water) and CO_2. Black line; dry [DBUH][Triz] (>0.1 wt% water). Pink line; dry [DBUH][Triz] (>0.1 wt% water) and CO_2.

A 90 °C isothermal was conducted to assess the rate of mass loss over the course of 300 minutes (5 hours) and 600 minutes (10 hours). It shows with an increased ΔpK_a of the cation and anion precursors ([Im]pK_a=14.52, [Triz]pK_a=9.89) the thermal stability increases, with a 20% increase of mass remaining after 5 hours for [DBUH][Triz] over the [DBUH][Im] system. [DBUH][Triz]+CO_2 has 32% mass remaining after 10 hours, the composition of this needs to be investigated further.

CO_2 Solubility in Protic ILs

As previously stated temperature, CO_2 partial pressure and water tolerance are major determining factors in the potential application in industrial CO_2 capture. Firstly, a CO_2 uptake experiment with respect to time was conducted to establish the optimal equilibration time meaning that the following uptake experiments would be allowed to equilibrate for the minimum time possible to reach thermodynamic equilibrium before further solubility studies were conducted.

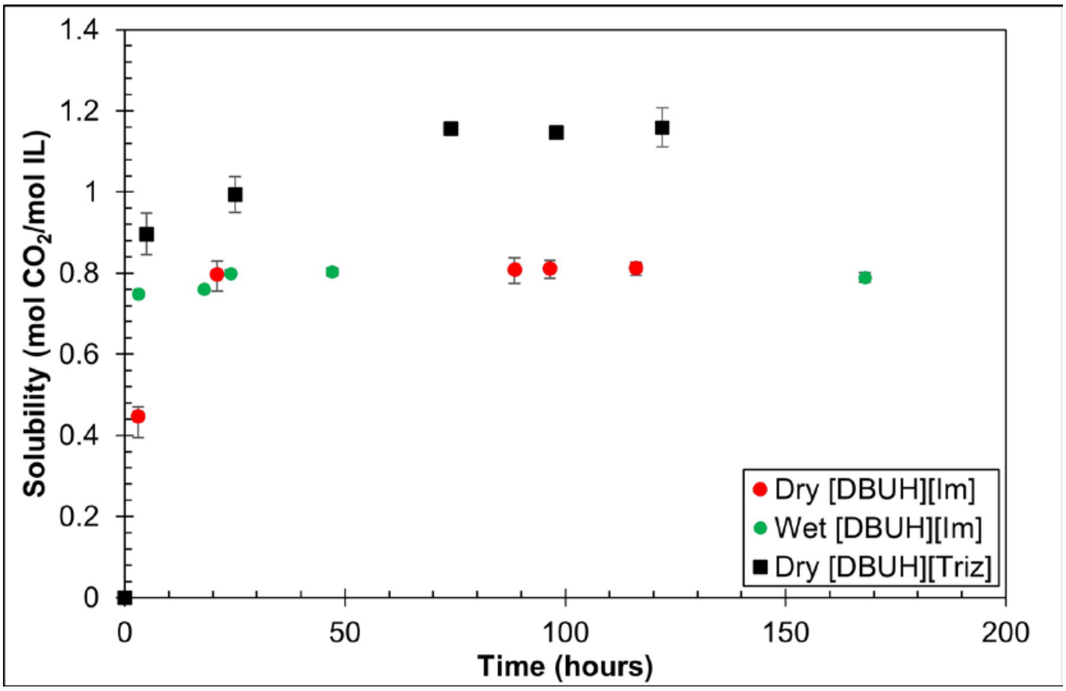

Figure 5 - Equilibration time for IL-CO_2 uptake at 35 °C. Red circle; 0.33 g of dry [DBUH][Im] (>0.1 wt% water), P_i=3000 mbar CO_2. Green circle; 0.37 g wet [DBUH][Im] (14 wt% water), P_i=3000 mbar CO_2. Black square; 0.2 g of dry [DBUH][Triz] (>0.1 wt% water), P_i=3500 mbar CO_2.

This can be seen for dry (>0.1 wt% water) [DBUH][Im] and wet (14 wt% water) [DBUH][Im] along with dry (>0.1 wt% water) [DBUH][Triz] as shown in Figure 5. Water tolerance is an important aspect for industrial CO_2 capture. There is no discernible difference in CO_2 uptake capacity between the dry and wet [DBUH][Im] when a water to IL molar ratio of 2:1 (which is equivalent to 14 wt%) is applied. The dry [DBUH][Im] has a capacity of 0.82 mol CO_2/mol IL and the wet [DBUH][Im] has a capacity of 0.80 mol CO_2/mol IL . However, when comparing the kinetics of absorption the dry [DBUH][Im] is slower than the wet [DBUH][Im] only reaching 0.44 mol CO_2/mol IL after 3 hours of stirring compared with 0.74 mol CO_2/mol IL for the wet [DBUH][Im] at the same time, in terms of % of the max solubility reached after 3 hours this is 54% and 93% for dry and wet [DBUH][Im] respectively. This could be due to the apparent lower viscosity of the [DBUH][Im] solution when water is added and will be verified through a rheology study in the future. When comparing [DBUH][Im] and [DBUH][Triz] there is a noticeable increase in the time the IL and CO_2 takes to equilibrate. For [DBUH][Im] maximum solubility is reached after 21 hours with no further increase from then onwards even after 116 hours (≈ 5 days). However [DBUH][Triz] maximum solubility is reached after 74 hours with no further increase from then onwards even after 122 hours (≈ 5 days). In terms of initial CO_2 uptake dry [DBUH][Triz] reaches 0.89 mol CO2/mol IL after 5 hours equivalent to 77% of the max solubility for this pressure. Wet [DBUH][Triz] is set to be investigated in the future with the expectation it will follow the same trend as the [DBUH][Im] system. These findings are consistent with the literature as Zhu et al[11,12] utilises a dynamic CO_2 uptake system bubbling the gas directly into the IL, for [DBUH][Im] a sharp uptake can be seen when the CO_2 solubility is displayed as a function of time compared to the same process for [DBUH][Triz] that shows a more rounded curve with gradual CO_2 uptake. The CO_2 solubility in the ILs are not comparable in Figure 5 due to the different initial pressured of CO_2 used, this was varied because of [DBUH][Triz]'s higher reported CO_2 uptake of 1.48 mol CO_2/mol IL.[11]

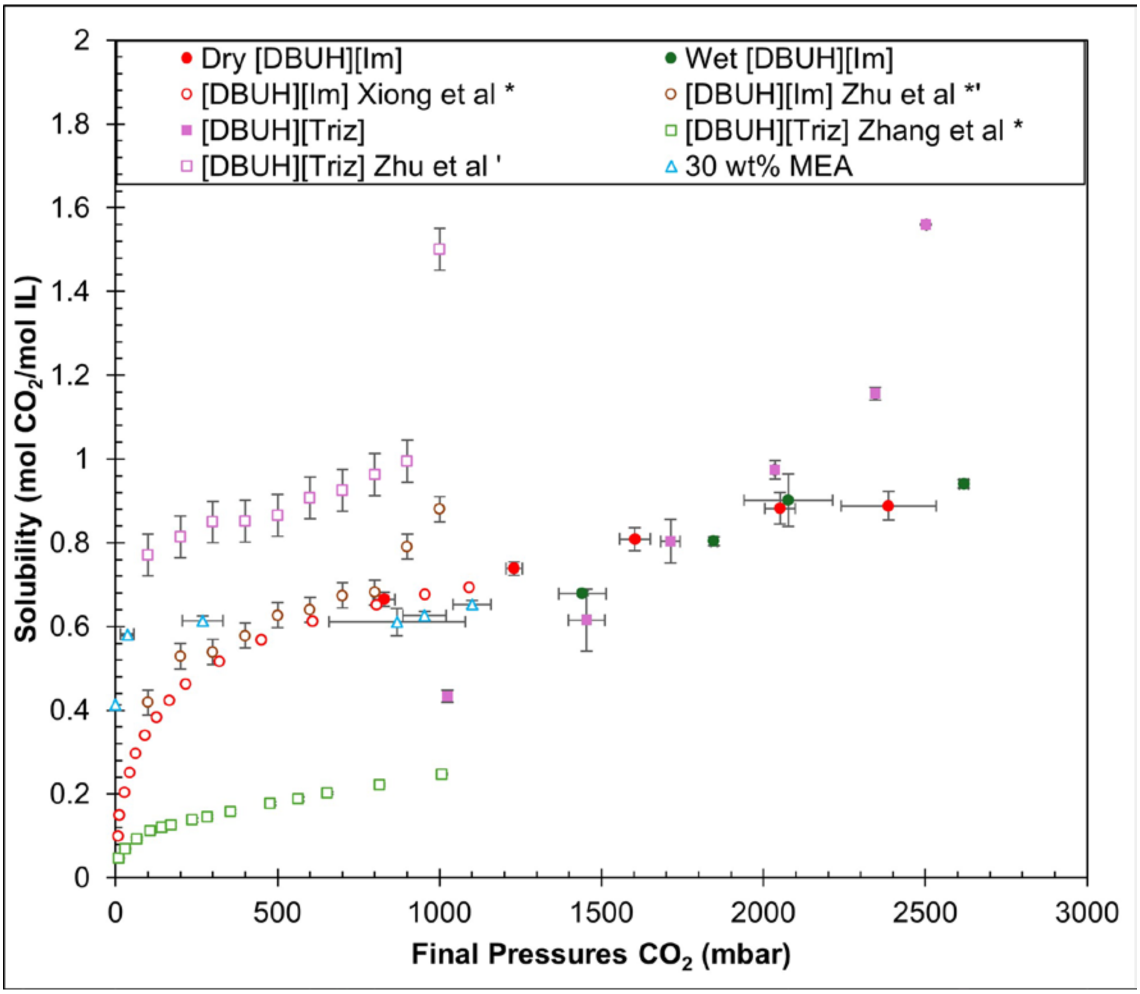

Figure 6 - CO_2 solubility in ILs at 35 °C in a static uptake system unless otherwise stated. * = uptake at 40 °C. ' = dynamic uptake system. Filled symbols are this work, unfilled symbols are from the literature. Red circle; 0.33 g of dry [DBUH][Im] (>0.1 wt% water). Green circle; 0.37 g wet [DBUH][Im] (14 wt% water). Red circle outline; [DBUH][Im] Xiong et al.[13] Brown circle outline; [DBUH][Im] Zhu et al.[14] Pink square; 0.2 g of dry [DBUH][Triz] (>0.1 wt% water). Green square outline; [DBUH][Triz] Zhang et al.[15] Pink square outline; [DBUH][Triz] Zhu et al.[11] Blue triangle outline; 1 g of 30 wt% MEA in water, Young et al.[16]).

CO_2 uptake varies as the concentration of CO_2 is increased. There is the apparent saturation of [DBUH][Im] at 0.9 mol CO_2/mol IL which matches the literature finding. The difference in pressure can be accounted for the difference in experimental set up as Zhu et al used a dynamic system with CO_2 in excess at ambient pressure. Whereas in the static system that we are using CO_2 is the limiting factor. As we increase the concentration of CO_2 in the headspace we can see matching solubilities. For [DBUH][Triz] there is a large difference in reported solubility however Zhang et al utilised a similar static system to ours and we have found that the equilibration time for [DBUH][Triz] to be 74 hours. Zhang et al did not report the time they allowed the system to equilibrate for and the system may still not be at equilibrium. Further investigation is planned for the [DBUH][Triz] system including a study to investigate the impact water has on [DBUH][Triz] – CO_2 uptake. The ILs outperform the MEA solution at concentrations of CO_2 but underperform at lower partial pressure.

Conclusions and future work

Increasing the ΔpK_a between cation and anion precursors increases the thermal stability of resulting protic IL. Screening of cation and anion to a large ΔpK_a to determine if there is a negative effect of CO_2 desorption with increasing ΔpK_a. High temperature CO_2 solubility and low CO_2 partial pressure are going to be examined in the gas-rig reactor.

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