QUEEN'S UNIVERSITY BELFAST

QUEEN'S UNIVERSITY IONIC LIQUID LABORATORIES
QUILL

QUILL
Quarterly Reports

February 2024 – April 2024

CONFIDENTIAL (up to April 2027)

Contents

QUILL Quarterly Report

February– April 2024

Name:	Haris Amir		
Supervisor(s):	Professor John Holbrey		
Position:	PhD student		
Start date:	10/01/2020	**Anticipated end date:**	09/2024
Funding body:	ESPRC/UKRI		

Designing New Halogen Free Borate Anions for Functional Applications

Background
New boron containing anions are of interest for the development of new ionic liquid anions with a wide range of potential applications including electro- and photo- chemistry, and for the separation and extraction of metals and waste. In this work, functional borate anions formed as complexes with O-, O/N-, and N- chelators for ionic liquid applications have been designed and investigated.

Thesis tile: Designing new halogen free borate anions for functional applications

Submission date: July 2024

Thesis structure:

Chapter list:

1. Introduction + literature review (under review – corrections to be made).
2. Synthesis & characterisation (completed).
3. sodium borate salts as electrolytes (under review – corrections to be made).
4. Conductivity of borate based ionic liquids (under review – corrections to be made).
5. Borate based Organic plastic crystals (OIPCs).
6. PDADMA FSI doped with sodium borate salts for solid state electrolytes (under review – corrections to be made).
7. Concluding remarks (under review – corrections to be made).

QUILL Quarterly Report

February 2024 – April 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. 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.

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

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

February 2024 – April 2024

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

Polyoxometalate-Based Electrode Catalysts for Improved Vanadium Redox Flow Battery Performance

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. The result was total saturation of fibres in crystals (fig. 1) which hindered the electrochemical performance of the felt as shown by cyclic voltammetry (fig. 2).

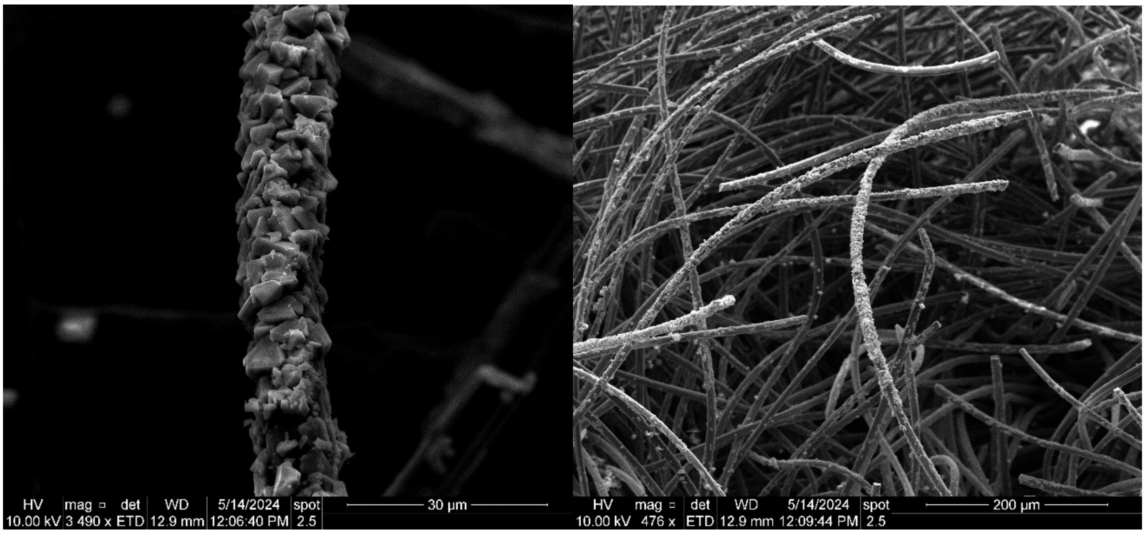


Figure 1 – SEM images of GF treated in 1M $[(n\text{-}C_4H_9)_4N]_2[Mo_60_{19}]$

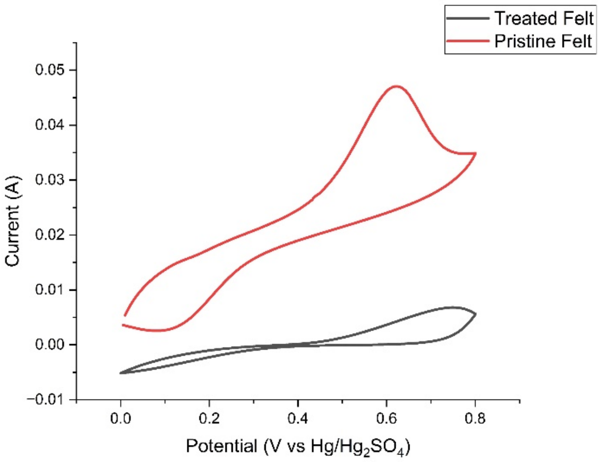


Figure 2 - Cyclic voltammograms of pristine and treated graphite felt in 0.01M $VOSO_4$/2m H_2SO_4 at a scan rate 10 mV/s^{-1}

It is theorised that the saturation of fibres negatively impacted the inherent conductivity to the carbon-based GF, to the detriment of the electrochemical activity of the electrode.

Conclusions and future work

To conclude, previous deposition of particles onto electrode surface was unsuccessful as it did not improve the performance. However, it is widely reported that the size, distribution nature and quantity of catalysts on the electrode surface play a key role in the electrochemical activity of the electrode. Therefore, reduced concentration of the treatment solution has been trialled with promising results. Further characterisation is necessary, both electrochemically and physically to probe the effect of lower concentration. Future investigations include the effect of treatment time, treatment temperature and treatment solution concentration on the deposition nature of the compound. Moving on form this, other POMs will be considered for investigation.

QUILL Quarterly Report

February – April 2024

Name:	Nia Foster		
Supervisor(s):	Dr Paul Kavanagh & Prof Peter 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. The limits are due to multiple factors, such as electrolyte degradation and the energy input required to maintain a very low potential. We require a technique that can raise the catalyst to a higher energy level while surpassing these limitations within the cell.

While these reactions involving electrolysis alone are successful, the electro-active catalysts are not very strong and sometimes require additional reactants such as acids or bases to activate harder-to-reduce species. 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 knowlegde 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. Therefore, we have decidied to carry out experiments to find three valuable properties that are able to explain why certain catalysts work better than others in certain situations. The properties are the redox potential, diffusion coefficient and apparent rate constant.

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.

The ideal catalyst would need to be electrochemically accessible, with the potential being more than 2.5V to produce the anion. It should have a fast diffusion through the electrolyte, ideally more than $10^{-6}cm^2s^{-1}$. The final attribute to make a good electrophotocatalyst is that it should be fast and reversible, with the heterogeneous electron transfer constant to be more than $10^{-3}s^{-1}$.

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 reporoduce. 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 of these factors we are ensuring we get the most accurate and reporducable results. Experiments are currently being carried out on a range of electrocatalysts to be able to provide a catelogue of catalysts and values for myself and other electrochemists to use.

Conclusions and future work

Once I have tested a wide range of these catalysts I am hoping to produce a paper that categorises these catalysts based off the three properties previously mentioned, that ideally will 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.

There are multiple areas of research that I could investigateI could possibly investigate different electrode materials and how effective they are with different types of electrocatalysts. A study could also be completed on different types of solvents or electrolytes, however, this project can go in many directions and holds lots of potential. I am also very interested in inorganic metal based electrocatalysts as I think that area holds a lot of potential.

QUILL Quarterly Report

February– April 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 3D-printable 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.

Conclusions and future work

Now CNC moulds have been manufactured, future work will manufacture multifunctional redox flow cell parts that can act as flow frames, current collectors, and electrode elements, whilst being linked by a continuous polymer matrix. Galvanostatic Charge/Discharge (GCD) will be done to test the manufactured parts in terms of energy efficiency.

QUILL Quarterly Report

February – April 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.

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.

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 Summer. I am currently writing the publication and analysing the results. 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-methylacridinium bistrifylimide/lutidine ionic liquid FLP, in preparation/anticipation of carrying out experiments at ISIS. In conclusion, the last bit of work that is planned for the next while is EIS spectroscopy on the C_3CNPyr[NTf_2] and C_4CNPyr[NTf_2] ILs and hence their mixes with 1-methylnaphthalene and after completion of the analyses of these ILs, we will move on to the 3,5-dicyanopyridinium ILs.

References

1. D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.,* 2010, 49, 46–76.
2. E. R. Clark and M. J. Ingleson, *Angew. Chem., Int. Ed.*, 2014, 53, 11306–11309.
3. Zhao H, Li Y, Zhu, X*ACS Omega.,* 2018, 3(10), 13598-13608.
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

February – April 2024

Name:	Sanskrita Madhukailya		
Supervisor(s):	Prof John D Holbrey and Dr Leila Moura		
Position:	PhD student		
Start date:	April 2021	**Anticipated end date:**	September 2024
Funding body:	Tezpur University-Queens University Belfast joint PhD programme		

LCST Behaviour in 5-Phenyltetrazolate Based Ionic Liquids

Background

In the previous report, deuteration of tetrabutylphosphonium bromide was attempted to prepare the D-ionic liquid for neutron scattering experiments. In addition to that, posters were presented at QUILL IAB and COIL-9 conference. Here, a brief summary of the phase behaviour results of the ionic liquid water mixtures with respect to crystal structures will be explained.

Objective of this work

The ultimate objective of this research is to comprehend and elucidate the phase behaviour of certain ionic liquids known as the lower critical solubility temperature (LCST), with the purpose of establishing the boundaries and formulating a methodology for synthesizing such ionic liquids that possess the potential to function as draw solutes in the forward osmosis process for desalinating seawater. During this procedure, a series of ionic liquids containing the tetrazole moiety will be synthesized, assessed, and compared to the current ones, considering the selection of the anion or cation, which can influence the phase behaviours.

Progress to date

1. Repeat the Phase behaviour tests to generate phase diagrams for the ionic liquids with substituents in the anions including $4CH_3$, $3CH_3$, $2CH_3$, $4C_2H_5$, $4CF_3$, 2Cl, 2Br, $4OCH_3$, and $3OCH_3$. It was observed that except the ionic liquid- water systems of 2Br, $4OCH_3$, and $3OCH_3$ substituted anions in the ionic liquid, all other systems displayed a phase diagram with undefined cloud point regions at lower compositions. This was mainly due to the presence of dispersed droplets and solids at lower temperatures. One such example is shown below:

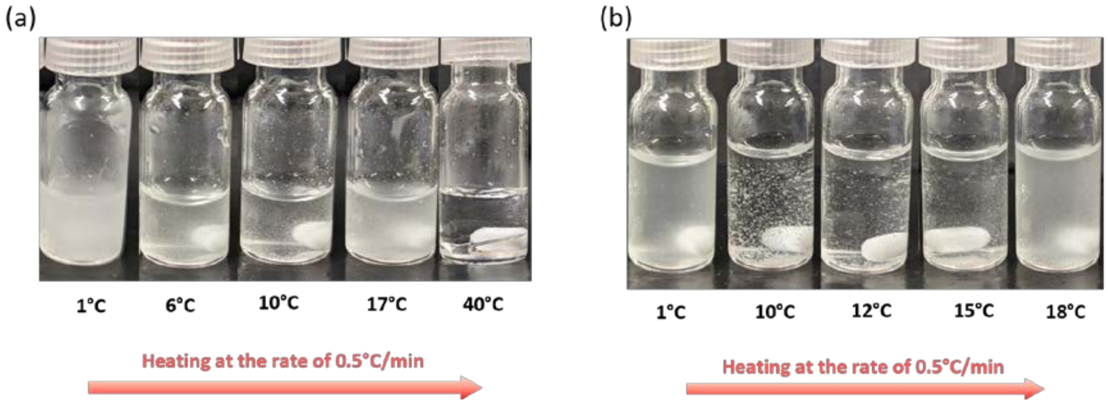
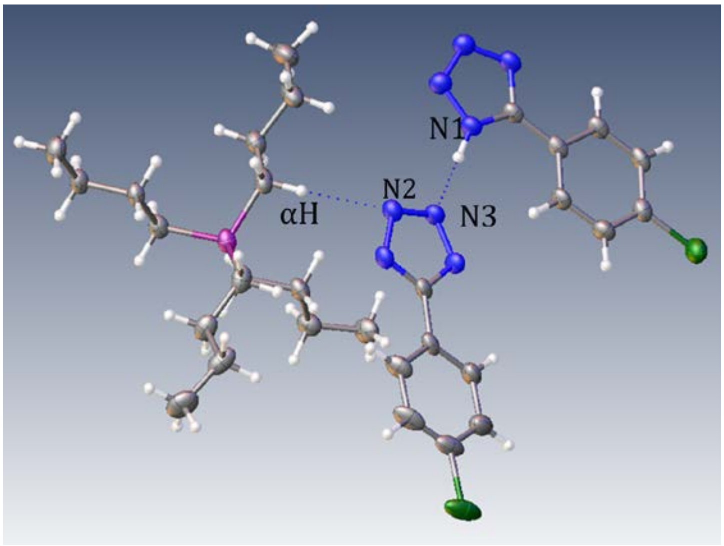
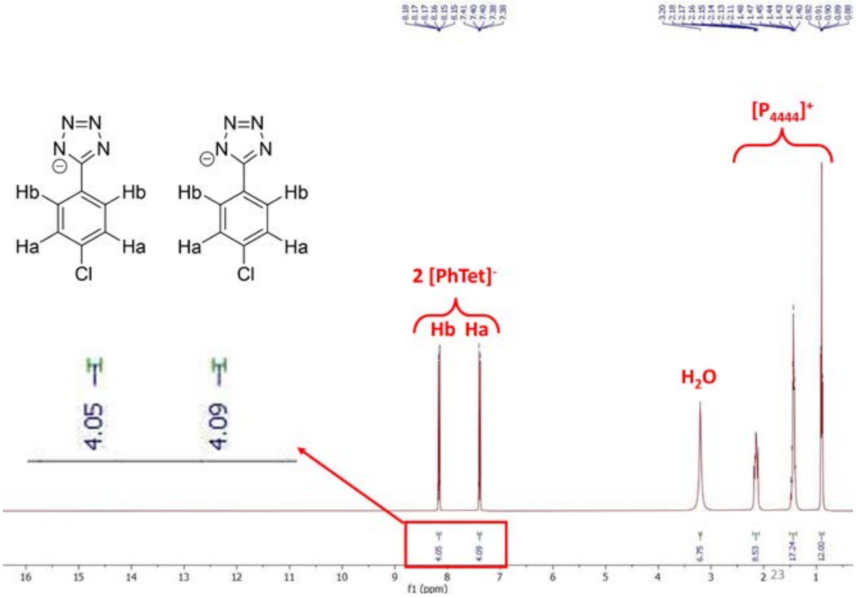


Figure 1 (a) 14.13wt% of $[P_{4444}][2CH_3Ph\text{-}Tet]$/H2O on a heating cycle. Droplets dispersed in the solution is observed at increasing temperatures (10 °C) which becomes cloudy at higher temperatures until phase separation at 40 °C; **(b)** 11.72wt% of $[P_{4444}][4CH_3Ph\text{-}Tet]$/H2O on a heating cycle. Solution is cloudy initially at 1 °C, on heating solids appear (10 °C) dispersed in the solution which turns into small droplets (12 °C) that further become cloudy on increasing temperatures until phase separation(not shown).

2. Crystal structure from 55.33wt% $[P_{4444}][4ClPhTet]/H_2O$ showing 1 cation-anion pair : H-bond between αH-N2 and 1 protonated 5- phenyltetrazole : H-bond between NH of the tetrazole and N3 of the tetrazolate anion.



3. ^{1}H-NMR of the crystals from 55.33wt% [P_{4444}][4ClPhTet]/H_2O in $CDCl_3$ showing two anion-like species in the crystal.



Conclusions and future work

1. Formation of non-stoichiometric species during crystal formation reported,
2. Undefined cloud point regions need to be investigated more,
3. Drafting a paper on the results so far on anionic functionalisation and LCST,
4. Repeating results for dicationic ionic liquid-water systems.

QUILL Quarterly Report

February– April 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

The bulk of the work complete in the last quarter centred on the development of a full-scale 3D COMSOL model with some of the main validation steps conducted previously. There have been many obstacles to overcome in developing this model to the required level, the primary difficulty being ensuring the stability of the model. Investigations are still ongoing as to the best method to overcome these issues. As the model is developed to remove the issues being faced a very early thesis draft has been assembled to more clearly define the narrative of the project.

Additionally, the development of the rig is ongoing, significant progress has been made on some of the constituent pieces of this with designs largely complete and some early physical assembly underway. The cell analogue that will accompany the rig is in its first round of prototyping after the theoretical design was finalised.

Conclusions and future work

The development of the COMSOL model and rig remain the focus of the project. The review paper is in its second round of internal review. The next step is to carry out physical tests on the cell analogue to confirm the properties achieved.

QUILL Quarterly Report

February– April 2024

Name:	Emma McCrea		
Supervisor(s):	Prof Gosia 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.

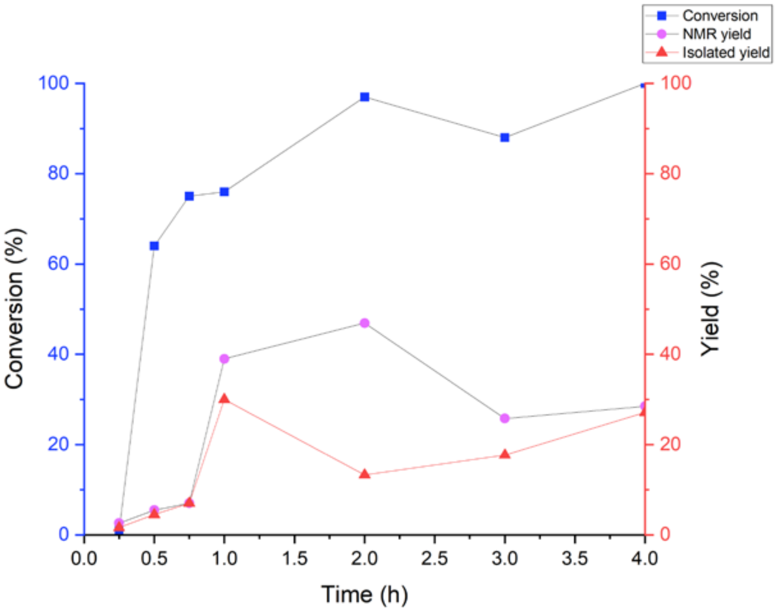
Ionic liquids, with their unique properties such as low volatility and tuneable chemical structures have emerged as versatile and efficient catalyst in various chemical processes. In the context of PET depolymerisation, the ionic liquids serve as catalysts, facilitating the breakdown of PET into DMT 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

February – April 2024

Name:	Kerri McKeever		
Supervisor(s):	Prof Gosia Swadzba-Kwasny & Prof John Holbrey		
Position:	PhD Candidate		
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 February and March, I continued on with data analysis of the soft XAS experiment we previously conducted in January, at beamline B07 at Diamond Light Source. This experiment involved studying many different boron-based compounds using soft x-rays and comparing them to the XRS data of the same compounds which was captured in February 2023 as well as comparing to simulations.

In February I also went to the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, where I aided in beamtime for Dr. Luke Higgins (Diamond), on the beamline ID20, with work into zeolites, using XRS to gain experience with using this beamline as I never got the opportunity previously. This also helped withdata analysis of my own work and we were able to remeasure the B K-edge of a compound, BCF which didn't not work the last time.

In the same month I continued to prepare for and had my Initial Progress Review (IPR) on the 13th February with Prof. Steven Bell.

In March, we had the biannual QUILL meeting, which I gave my first presentation and poster at. I also spent the month preparing for this event.

Furthermore, I synthesised more $[d_8\text{-}P_{66614}][NTf_2]$ which I had made previously, but we had a meeting with our collaborators and we released we needed to run more analysis and therefore needed more so I spent some time remaking this sample.

Additionally, I spent time attempting to synthesise BcatBu, a boron compound which we had measured using XRS but not using soft XAS so we aimed to apply to Rapid Access in Diamond Light Source, to measure these two compounds and have a complete set of samples. This synthesis was tricky, we attempted using Dean-Stark apparatus but the solvent and product had such similar boiling points, it was difficult to purify, eventually we found another method which was successful. I also wrote the proposal for the Rapid Access beamtime.

In April, I attended the ISIS Disordered Materials User Meeting at Cosner's House with Leila, Michael and Aodhan. It was a 4 day event where people gave presentations on their work and there was also a workshop for the two data processing software: DISSOLVE and EPSR which I attended the former. It was very informative and gave us good insight into this. DISSOLVE is a software which I will be using throughout the course of my PhD.

Moreover, I continued with the analysis of the XAS data as well as the X-ray Raman Spectroscopy (XRS) data which was captured at the ESRF back in February 2023, using python.

Conclusions and future work

I have attended beamtime at the ESRF, a User meeting for ISIS and the QUILL meeting, I completed synthesis of different compounds and my Initial Progress Review and I have continued to analyse the data captured form X-ray Synchrotron experiments which I will continue to do so.

Going forward, I will be preparing from my Differentiation, conducting synthesis of a range of isotopically pure compounds for an upcoming ISIS experiment, and prepare for upcoming trips for a Diamond data analysis workshop and user meeting, and ISIS deuteration user meeting, as well as applying fro Rapid Access for the 2 additional samples which I have made.

QUILL Quarterly Report

February – April 2024

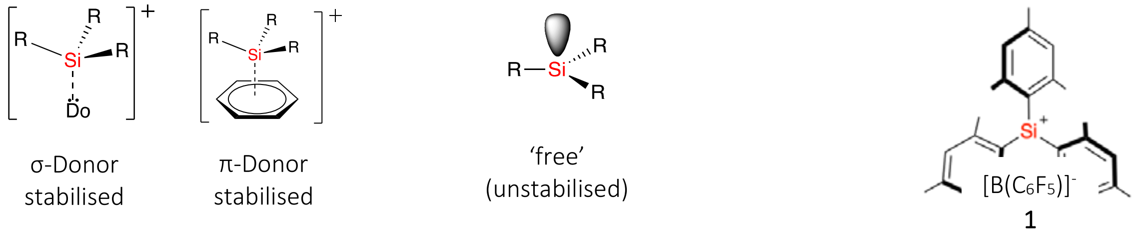
Name:	Shannon McLaughlin		
Supervisor(s):	Professor Gosia Swadźba-Kwaśny		
Position:	PhD Student (4th year)		
Start date:	October 2020	**Anticipated end date:**	June 2024
Funding body:	Department for the Economy (DoE)		

Ionic Liquids Based on Silicon Cations

Background

The chemistry of Lewis acidic main group cations is of increasing importance, as metal-free catalysis gains interest of the scientific community. One of the longest-standing challenges in main group synthetic chemistry has been the preparation of tricoordinate, tetravalent silicon cations in the condensed phase. Silylium ions are extremely Lewis acidic and have a high electrophilicity, oxophilicity and fluorophilicity, affording unique transformations that cannot be performed by traditional metal catalysts. Recently, synthetic methods to generate stable silylium cations have become more accessible and more effective.

Silylium ions can be categorised as either stabilised or 'free' (Figure 1a). As they are highly reactive, silicon cations are commonly found as species which are stabilised, whereas 'free' silicon cations are extremely rare. The first ever 'free' silylium cation to be isolated was the trimesitylsilylium cation ($(Mes)_3Si^+$) illustrated in Figure 1b.[1] Silylium ions are usually quite a reactive species but the bulky mesityl groups in compound **1** help to shield the silicon centre from attack by large nucleophiles. These steric interactions also prevent the silylium ion reacting with the solvent and the product alkene making it much more stable. The tridurylsilylium cation ($(duryl)Si^+$)[2] was later isolated along with the related species $(C_6Me_5)_3Si^+$.[3] Till date these three compounds are the only examples of 'free' species whose structures have been confirmed by X-ray crystallography.



1

Figure 1 a) Example structures of stabilised and unstabilised silylium ions. b) Structure of 'free' trimesitylsilylium cation.

Objective:

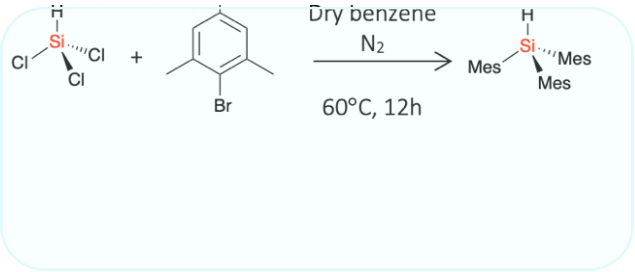
This work reports on the first-ever attempt to prepare and characterise silylium ionic liquids. The first goal of this project is to synthesise the 'free' trimesitylsilylium cation illustrated in Figure 1b.

Progress to date:

Synthesis of trimesitylsilane:

Trimesitylsilane was synthesised following the method described by Lappert *et al.*[4] 0.74 g of trimesitylsilane was synthesised (white crystals shown in Figure 2). A second batch of trimesitylsilylium was synthesised to increase the yield. ^1H, ^{13}C and ^{29}Si NMR spectra for trimesitylsilane were recorded. Peaks observed matched exactly to literature values in all NMR spectra.

Scheme 1 - Synthesis of trimesitylsilane.

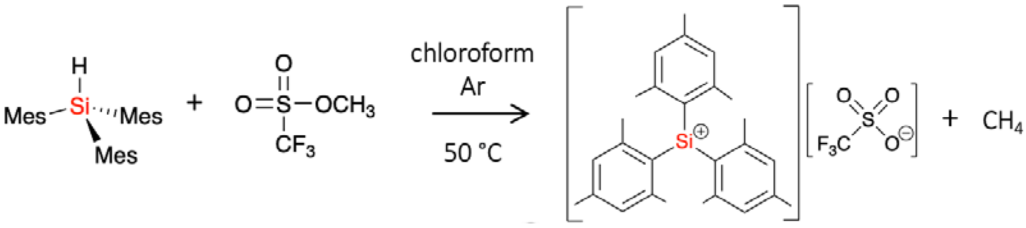


Lappert *et al.*[4]

Figure 2 - White crystals of trimesitylsilane, first batch (left) and second batch (right).

Synthesis of [Si(Mes)$_3$][OTf]:

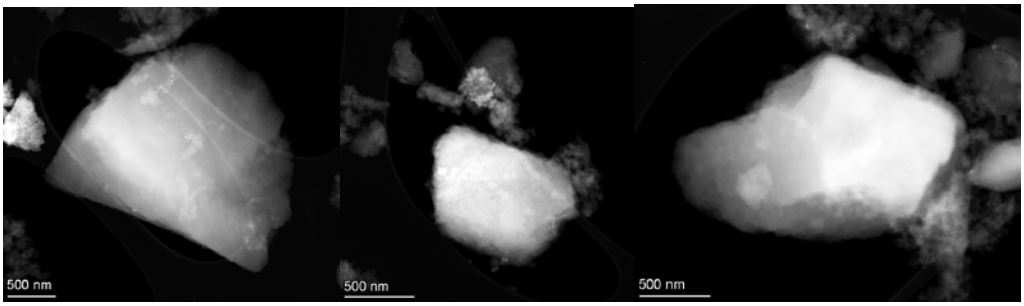
Scheme 3 - Synthesis of [Si(Mes)$_3$][OTf].



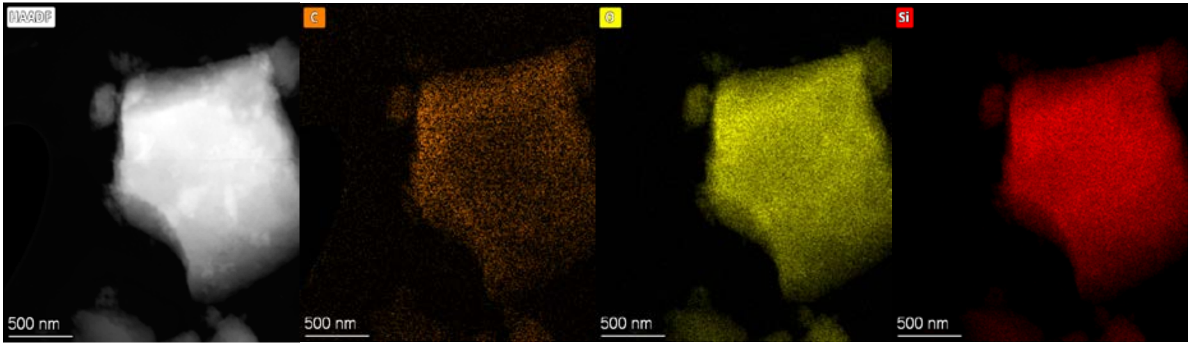
The synthetic route, illustrated in Scheme 3, was proposed to generate trimesitylsilylium trifluoromethanesulfonate (triflate), [Si(Mes)$_3$][OTf]. The trimesitylsilane starting material will be reacted with methyl trifluoromethanesulfonate (Me[OTf]) and refluxed under argon in chloroform at 50 °C. The progress of the reaction was monitored using ^{1}H, ^{13}C and ^{29}Si NMR.

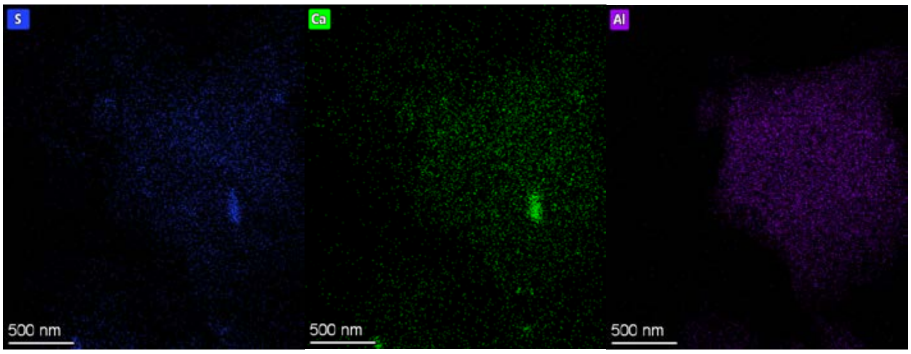
Conclusions

A sample of [Si(Mes)$_3$][OTf] was submitted for analysis using Transmission Electron Microscopy (TEM). Mainly large particles of irregular shapes were found. Qualitative elemental maps were recorded, and quantitative analysis was used to determine the elemental composition of the sample.

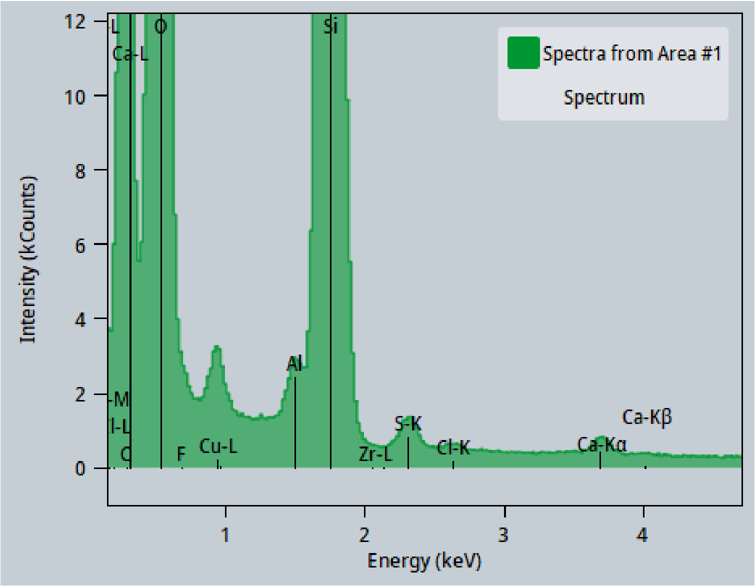


Qualitative Elemental Maps:



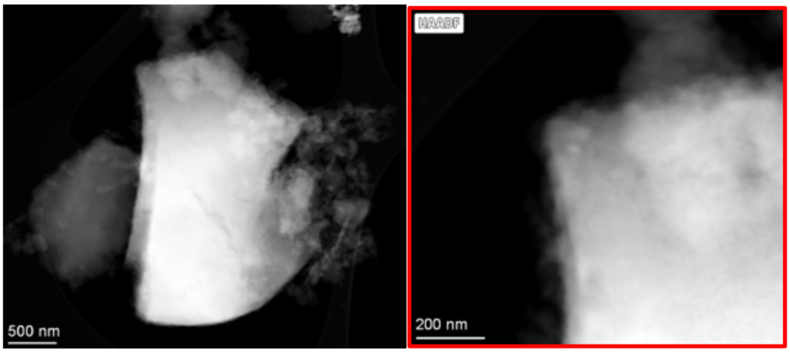


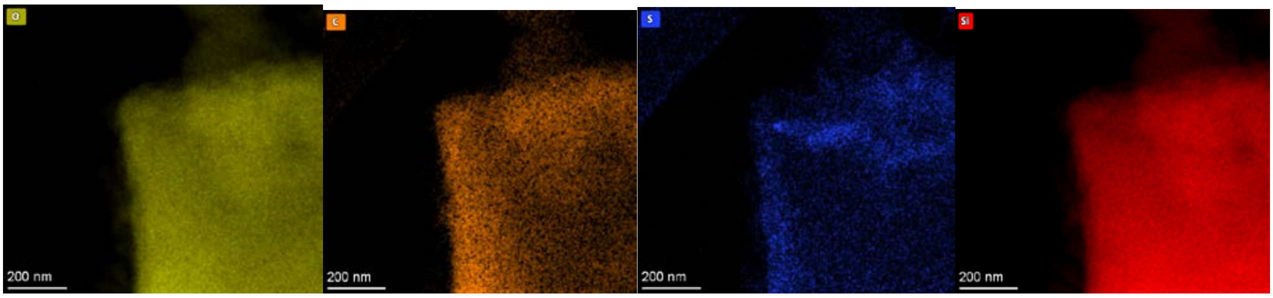
Elements present:
- ● carbon
- ● oxygen
- ● silicon
- ● sulfur
- ● calcium
- ● aluminium

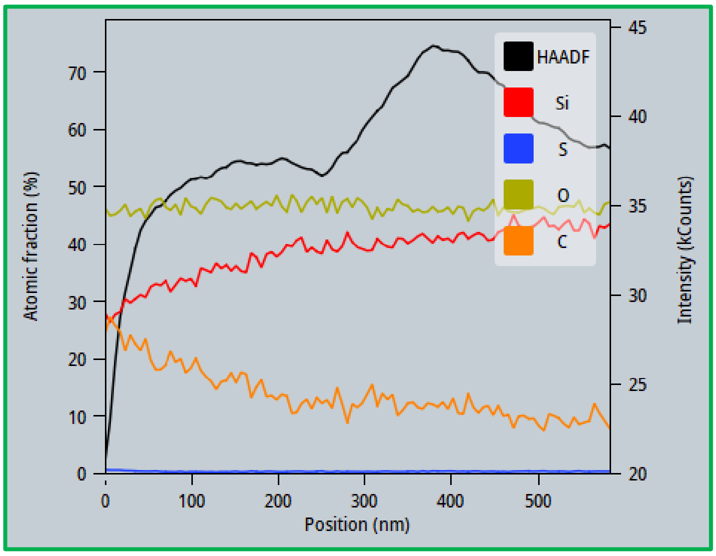


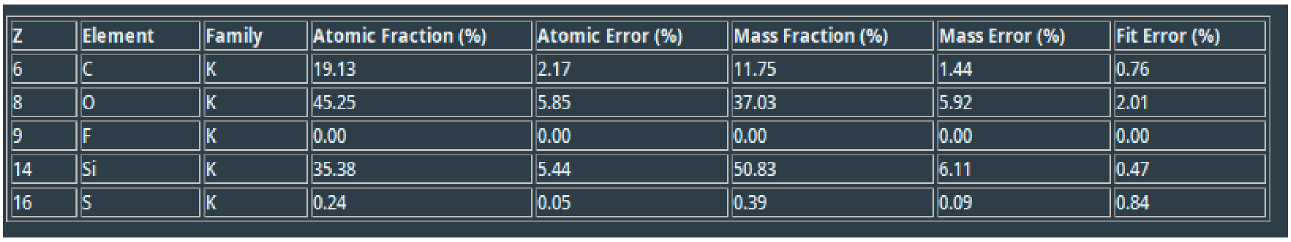
The elemental distribution is homogeneous, although in some areas agglomeration of sulfur (S) and calcium (Ca) was identified. Signals for calcium (Ca) and aluminium (Al) may be due to cross-contamination from glassware during sample preparation and handling. The dwell time varied from 5 to 30 milliseconds.

Quantitative Analysis:





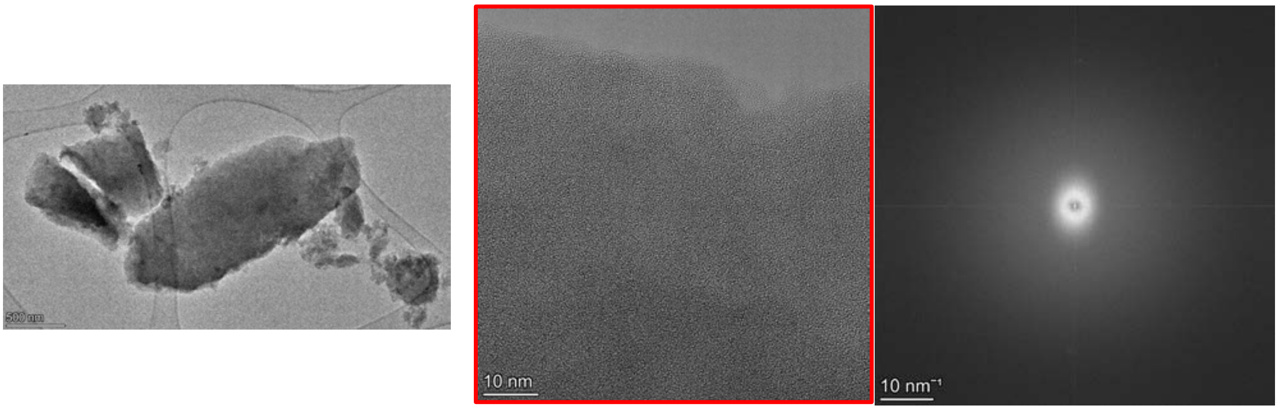




Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit Error (%)
6	C	K	19.13	2.17	11.75	1.44	0.76
8	O	K	45.25	5.85	37.03	5.92	2.01
9	F	K	0.00	0.00	0.00	0.00	0.00
14	Si	K	35.38	5.44	50.83	6.11	0.47
16	S	K	0.24	0.05	0.39	0.09	0.84

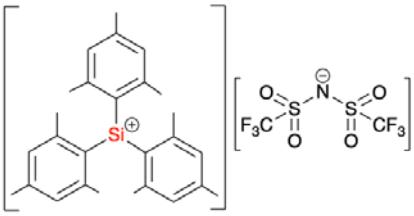
Bright Field TEM:

No crystalline structure was identified.



Future work

Future work will involve submitting a sample of [Si(Mes)$_3$][NTf$_2$] for TEM analysis. Qualitative elemental maps will be recorded and quantitative analysis will be used to determine the elemental composition of the sample. Bright field TEM will also be used to identify if there is any crystal structure present.



[Si(Mes)$_3$][NTf$_2$]

References

1. K. C. Kim, C. A. Reed, D. W. Elliott, L. J. Mueller, F. Tham, L. Lin and J. B. Lambert, *Science.*, 2002, **297**, 825–827.
2. J. B. Lambert and L. Lin, J. Org. Chem., 2001, **66**, 8537–8539.
3. A. Schäfer, M. Reißmann, S. Jung, A. Schäfer, W. Saak, E. Brendler and T. Müller, Organometallics, 2013, **32**, 4713-4722.
4. M. J. S. Gynane, M. F. Lappert, P. I. Riley, P. Rivière and M. Rivière-Baudet, J. Organomet. Chem., 1980, **202**, 5-12.

QUILL Quarterly Report

February– April 2024

Name:	Beth Murray		
Supervisor(s):	Prof Gosia Swadźba-Kwaśny & Prof John Holbrey		
Position:	PhD student		
Start date:	October 2022	**Anticipated end date:**	October 2025
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]

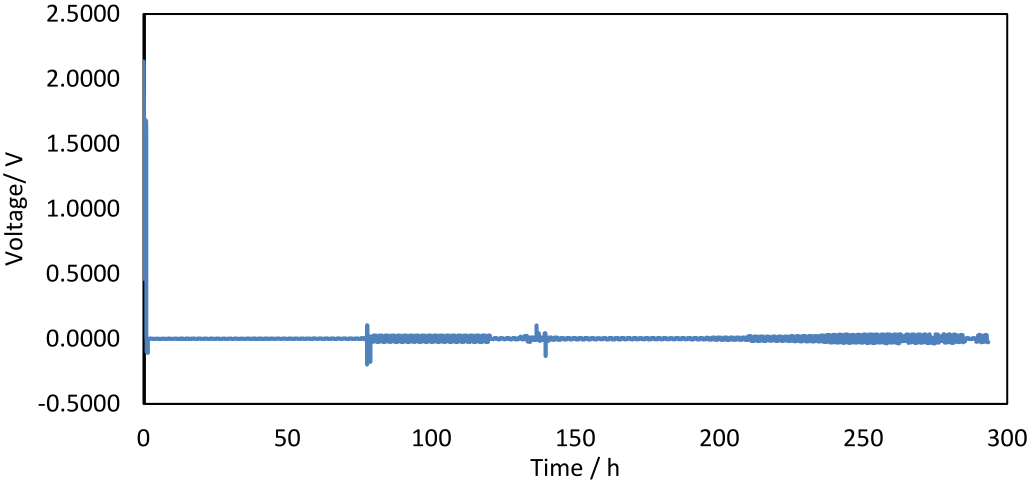


Figure 1 - Galvanostatic cycling of Al/Al symmetrical cell with urea-$AlCl_3$ electrolyte.

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).

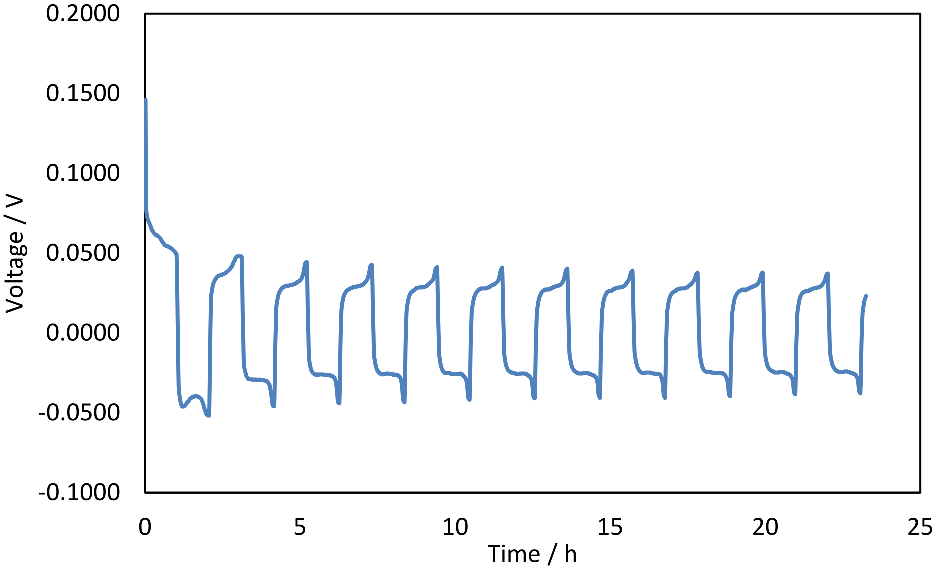


Figure 2 - Galvanostatic cycling of Al/Al symmetrical cell with urea-$AlCl_3$ electrolyte, after the Al electrodes were polished with acid.

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).

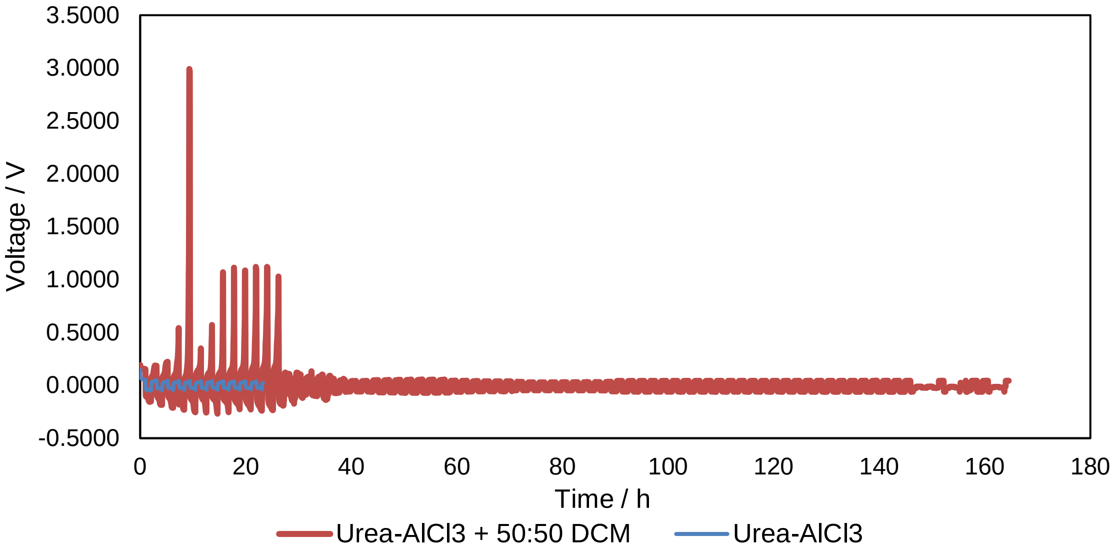


Figure 3 - Comparison of symmetrical Al/Al cycling with urea-$AlCl_3$ electrolyte and urea-$AlCl_3$ electrolyte with the addition of equimolar amounts of DCM

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. 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.

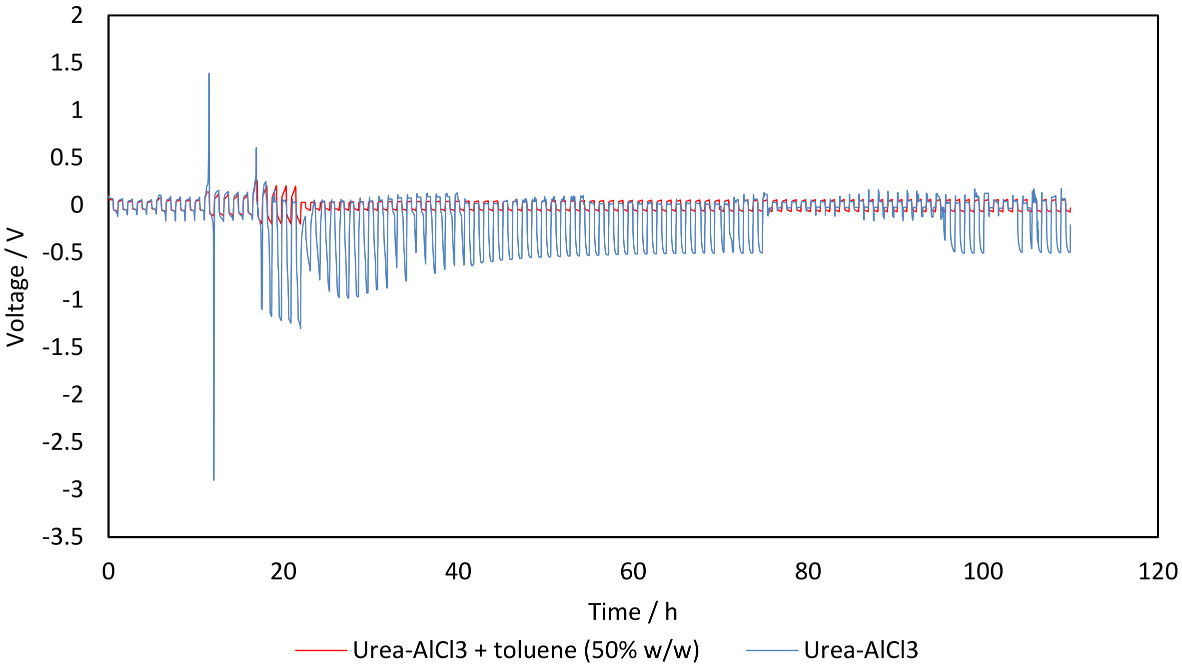


Figure 4 - Comparison of symmetrical Al/Al cycling with urea-$AlCl_3$ electrolyte and urea-$AlCl_3$ with the addition of toluene (50% w/w).

As mentioned earlier, a coin cell configuration was utilized 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,[15] 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,[16] 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, the LCC containing toluene and neat toluene. Figure 5 shows the comparison of each Raman spectra, clearly showing the addition of toluene affects the structure of the neat LCC. The peaks labelled from the urea-AlCl3 spectra correspond to different aluminium species. When toluene is added the peaks disappear, signalling that the Al-Cl and Al-O bonds are broken. Interestingly, the Raman spectra of the LCC with varying amounts of toluene (25%-75%) exhibited no discernible differences. This observation suggests that even small quantities of toluene can disrupt the structure, and the added quantity does not have a distinguishable effect.

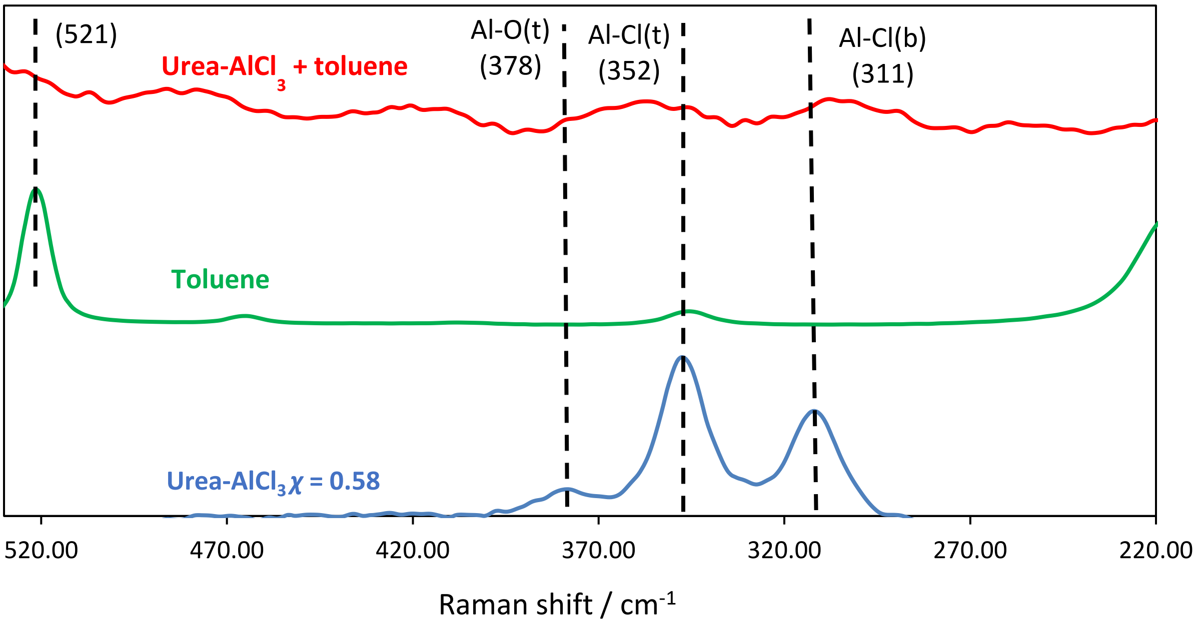


Figure 5 - Comparison of the Raman spectra for urea-AlCl3 LCC, urea-AlCl$_3$ LCC with toluene and neat toluene.

Figure 6 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.

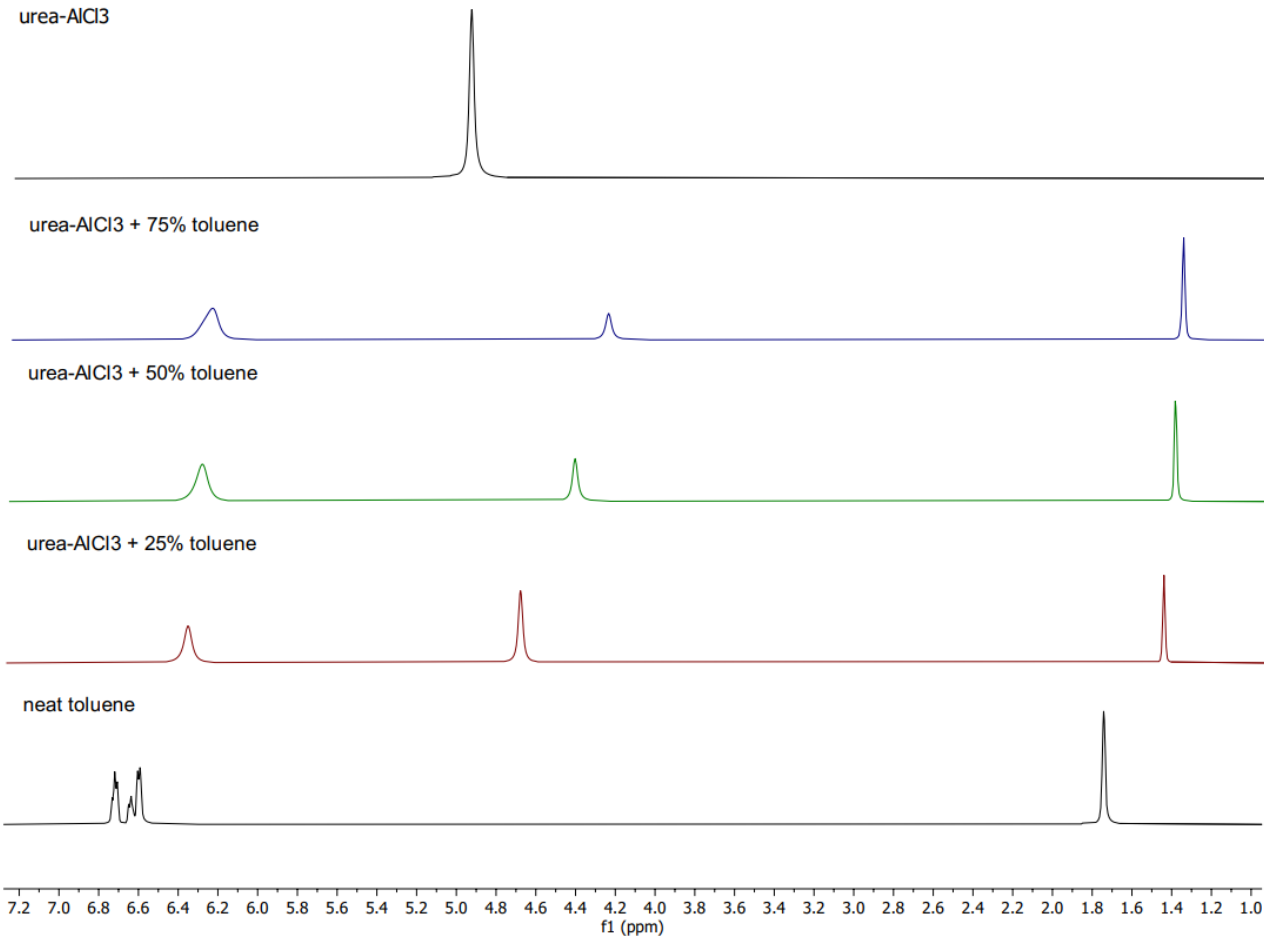


Figure 6 - ^{1}H NMR comparison of urea-$AlCl_3$ with toluene (25%, 50% and 75%) with neat urea-$AlCl_3$ and neat toluene. NMR solvent: d_6-DMSO (capillary).

Figure 7 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.

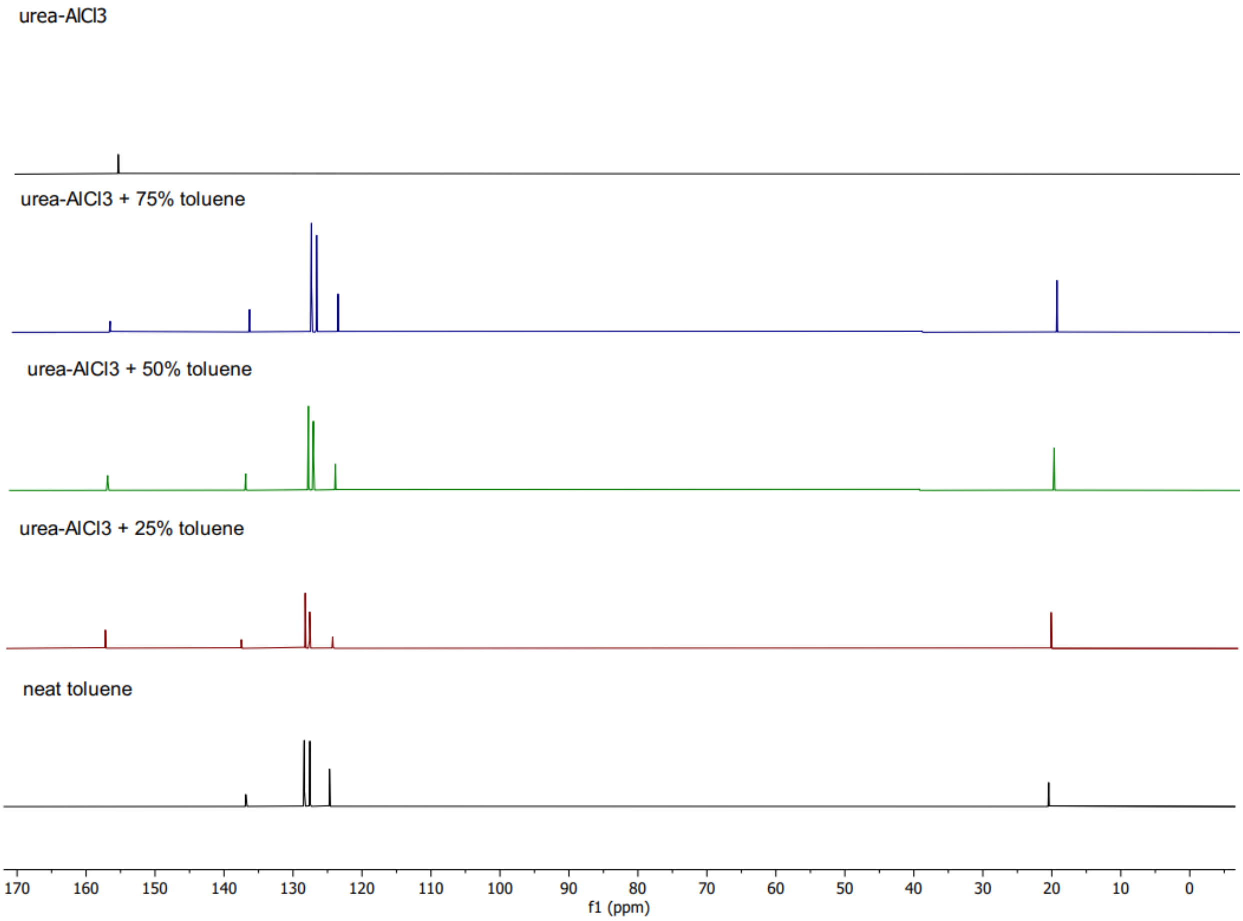


Figure 7 - ^{13}C NMR comparison of urea-$AlCl_3$ with toluene (25%, 50% and 75%) with neat urea-$AlCl_3$ and neat toluene. NMR solvent: d_6-DMSO (capillary).

In order to study the coordination environment of aluminium in the LCC when toluene was added, ^{27}Al NMR was carried out (Figure 8). 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.

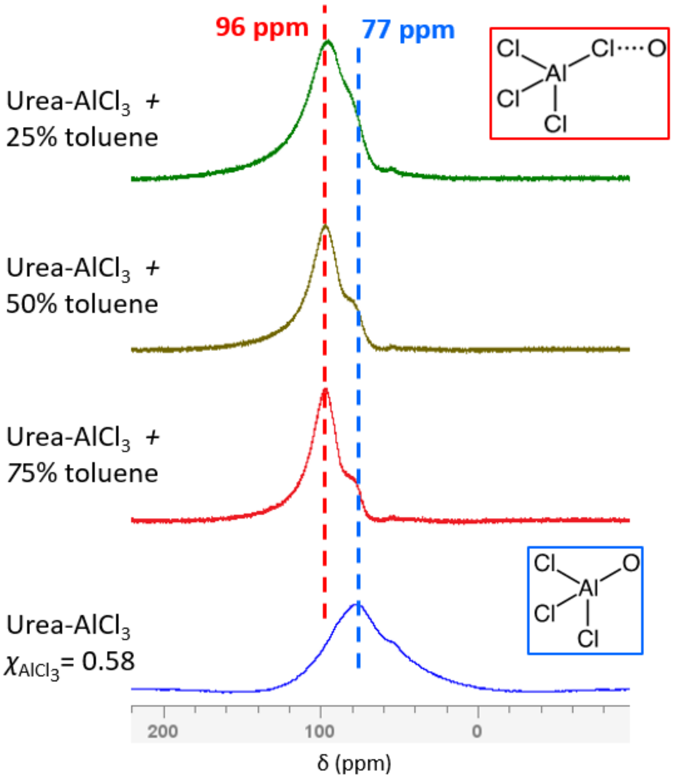


Figure 8 - ^{27}Al NMR comparison of urea-$AlCl_3$ with toluene (25%, 50% and 75%) with neat urea-$AlCl_3$ and neat toluene. NMR solvent: d_6-DMSO (capillary).

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. In order to achieve better understanding of the speciation, the NMR experiments are going to be repeated using methylcyclohexane instead of toluene, hopefully allowing us to determine if the p-orbitals of the double bonds in toluene are affecting the speciation. 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.

References

1. E. Commision, *COMMISSION STAFF WORKING DOCUMENT - Energy storage – the role of electricity*, 2017.
2. S. K. Das, S. Mahapatra and H. Lahan, *J. Mater. Chem.*, 2017, **5**, 6347-6367.
3. J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359-367.
4. C. Julien, A. Mauger, A. Vijh and K. Zaghib, in *Lithium Batteries: Science and Technology*, eds. C. Julien, A. Mauger, A. Vijh and K. Zaghib, Springer International Publishing, Cham, 2016, pp. 29-68.
5. G. A. Elia, K. Marquardt, K. Hoeppner, S. Fantini, R. Lin, E. Knipping, W. Peters, J.-F. Drillet, S. Passerini and R. Hahn, *Adv. Mater.*, 2016, **28**, 7564-7579.
6. P. Eiden, Q. Liu, S. Zein El Abedin, F. Endres and I. Krossing, *Chem. Eur. J.*, 2009, **15**, 3426-3434.
7. N. M. Rocher, E. I. Izgorodina, T. Rüther, M. Forsyth, D. R. MacFarlane, T. Rodopoulos, M. D. Horne and A. M. Bond, *Chem. Eur. J.*, 2009, **15**, 3435-3447.
8. H. M. A. Abood, A. P. Abbott, A. D. Ballantyne and K. S. Ryder, *Chem. Commun.*, 2011, **47**, 3523-3525.
9. F. Coleman, G. Srinivasan and M. Swadźba-Kwaśny, *Angew. Chem. Int. Ed.*, 2013, **52**, 12582-12586.
10. K. Ueno, J.-W. Park, A. Yamazaki, T. Mandai, N. Tachikawa, K. Dokko and M. Watanabe, *The Journal of Physical Chemistry C*, 2013, **117**, 20509-20516.
11. Y. Zhao and T. VanderNoot, *Electrochim. Acta*, 1997, **42**, 1639-1643.
12. M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nature Materials*, 2009, **8**, 621-629.
13. X.-G. Sun, Y. Fang, X. Jiang, K. Yoshii, T. Tsuda and S. Dai, *Chem. Commun.*, 2016, **52**, 292-295.
14. M. Angell, C.-J. Pan, Y. Rong, C. Yuan, M.-C. Lin, B.-J. Hwang and H. Dai, *Proceedings of the National Academy of Sciences*, 2017, **114**, 834-839.
15. M. Angell, G. Zhu, M.-C. Lin, Y. Rong and H. Dai, *Adv. Funct. Mater.*, 2020, **30**, 1901928.
16. A. Bakkar and V. Neubert, *Electrochim. Acta*, 2013, **103**, 211-218.

QUILL Quarterly Report

February – April 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 standard.

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 ^{0}C to release the CO_2.[9] Couple this with the mass loss at the operating temperatures, it's a system fit for redesign.

Different attempts have been employed in reducing the amount of water with other solvents and added organic solvents to mitigate the shortcomings of the water 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 captures CO_2 through chemisorption, it binds the CO_2 to form the carbamate byproduct and regenerates with CO_2 release upon heating as can be seen in figure 2 and the schematic outline of the scrubbing set up in figure 3.

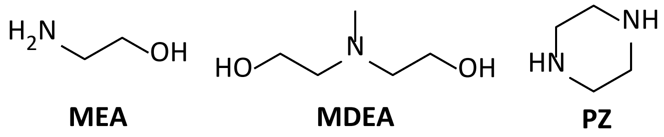


Figure 1 - Common amine structures

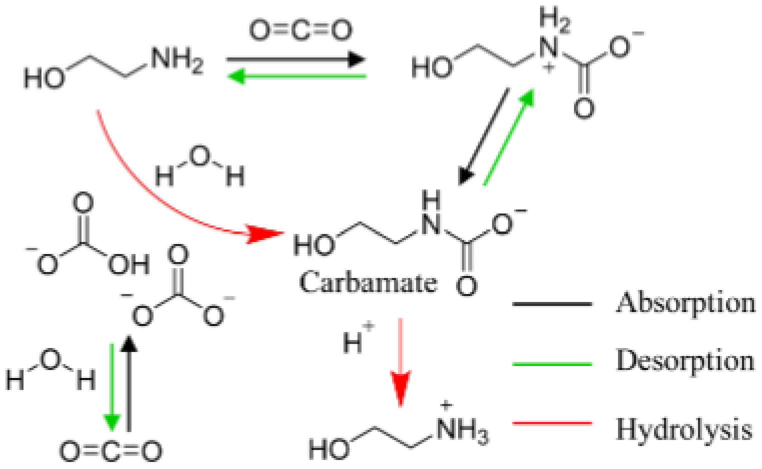


Figure 2 - Reaction pathway for MEA & CO_2[11]

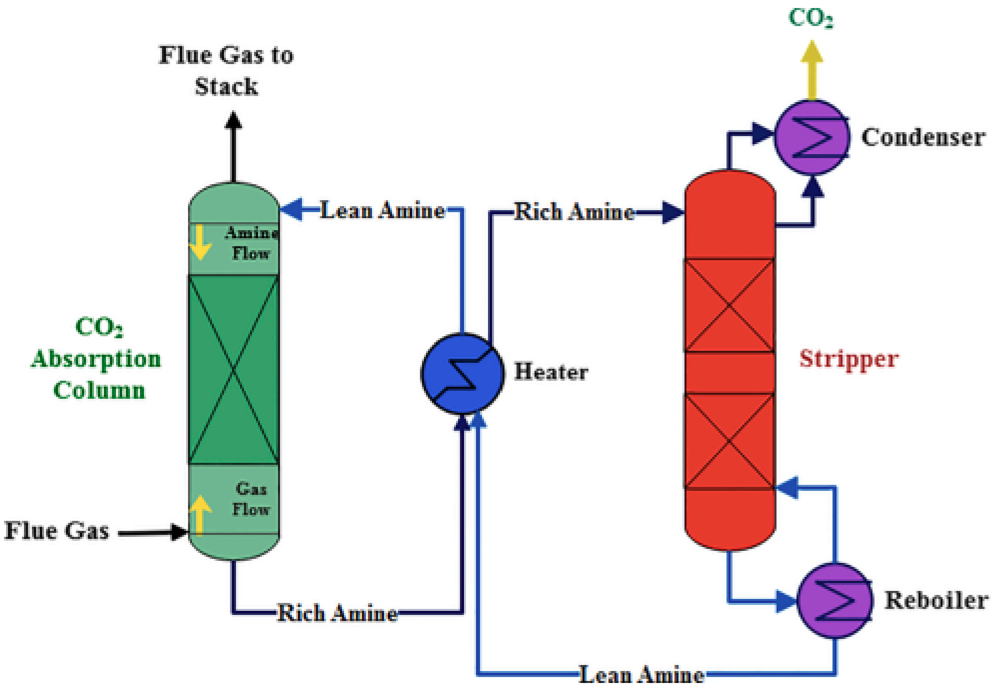


Figure 3 - Schematic diagram of a typical amine scrubbing system.[12]

One such potential replacement is 1,8-Diazabicyclo[5.4.0]undec-7-ene imidazolate [DBUH][Im] (structure shown in figure 4). Previous work done through QUILL had used gravimetric analysis to determine the CO_2 capacity at elevated absorption temperatures and the role water plays in the mechanism of absorption.

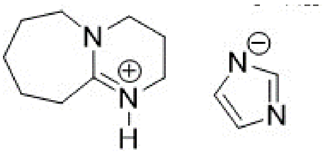


Figure 4 - [DBUH][Im]

Objective of this work

The main objective of this project is to capture carbon dioxide (CO_2) from commercial process streams namely flue gas, using ionic liquids (ILs) or analogue materials. Flue gas is the exhaust from industrial processes from oil refinery.

Progress to date

- Update on the septa for the GC.

The septa used in the screening method for gas absorbance designed within the Moura group[13] have been discontinued. The screening method utilises a sealed system comprising of a vial & septum that are crimped closed and measured via GC with column designed for permanent gases. The method uses an initial calibration curve of the empty vial and correlates the number of moles present at a known temperature and pressure with the peak area given from the GC. An absorbent is added and to vial and the headspace is filled with a known amount of moles of gas and left to equilibrate. The final number of moles in the headspace is determines from the GC peak area and relates back to the calibration curve. The absorbed moles are simply the initial moles minus the final moles. The method replies on the premise that the system is sealed, and the septum plays a crucial part in that assumption.

The search for a replacement septum spanned a wide variety of companies as can be seen in table 1. An initial test was conducted with 3000 mbar of CO_2 and snoop was placed over the puncture hole to see if it leaked as could be witnessed with the production of bubbles. As can be seen in table 1 many septa failed to have sufficient resealing capability even though they were advertised as such. Eventually an acceptable septum was sourced with the PTFE side pointing upwards.

Test #	Company	Material	Shape	Snoop Test	Calibration
Current	Perkin Elmer	Bromo butyl rubber	Standard Domed shape	Pass	Pass
1	Agilent	Bromo butyl rubber	Standard Domed shape	Fail	-
2	ESSLAB	Bromo butyl rubber	Standard Domed shape	Fail	-
3	Thermo-Fisher	Bromo butyl rubber	Standard Domed shape	Fail	-
4	ESSLAB	Bromo butyl rubber	Standard Domed shape	Fail	-
5	Fisher Scientific	Butyl Rubber	Weirdly Domed	Fail	-
6	Amazon	Butyl Rubber	Standard Domed shape	Fail	-
7	Borrowed*	Silicone-PTFE (PTFE skywards)	Flat	Fail	-
8		Silicone-PTFE (Silicone skywards)		Fail	-
9	Perkin Elmer	Butyl-PTFE.	Flat	Fail	-

		(Butyl skywards)			
10		Butyl-PTFE. (PTFE skywards)		Pass	Pass
11	Agilent	Butyl-PTFE. (Butyl skywards)	Flat	Fail	-
12		Butyl-PTFE. (PTFE skywards)		Pass	Pass

Table 1 - Replacement Septa Overview

Following on from a successful snoop test the septa then underwent a calibration curve produced immediately and another left resting for 1 week to determine if there were any leaks from the sides of the septa and the glass. Two septa were tested using this method both made from a PTFE/Butyl rubber blend. There is no substantial different in the calibration curves between both time periods, showing that there is a sufficient seal on the septa. The same set of calibration were conducted with the Perkin Elmer PTFE/Butyl septa and similarly showed no leak but due to a large cost difference Agilent was selected to go forward.

- Ionic Liquid CO_2 Capture

1,8-Diazabicyclo[5.4.0]undec-7-ene imidazolate [DBUH][Im] (structure shown in figure 4) was tested for optimal CO_2 equilibrium time to determine when the thermodynamic equilibrium had been reached, as can be seen in figure 5. The IL shows no further gas uptake after the 21st hour mark compared to the 120th hour mark. This shows that the reaction has reached thermodynamic equilibrium at this point.

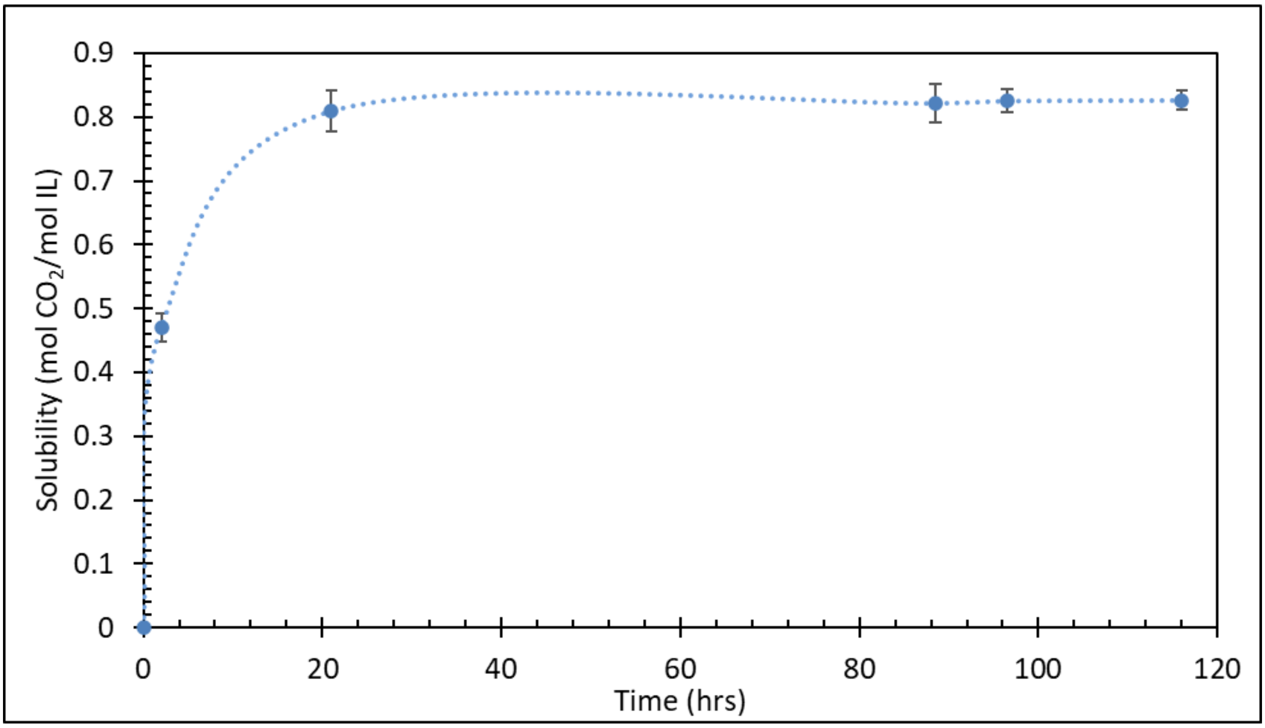


Figure 5 - Equilibrium time, 0.33 g of IL were filled with 3000 mbar of CO_2 and left in a 35 ^{0}C oil bath to determine the solubility increase over time

[DBU][Im] was then tested with different initial pressures of CO_2 (2000, 2500, 3000, 3500, 4000 mbar) (figure 6) by the GC method[13] , each datapoint represents 3 pressurised 20 ml vials with 0.33 g of IL inside. Literature capacity have reported 0.68 (mol CO_2/mol IL)[14] and 0.9 (mol CO_2/mol IL)[15] both using gravimetric bubbling experiments at atmospheric pressure, with the 0.9 (mol CO_2/mol IL) optimizing the flow rate to 2 L/min. We can see an overlap with both the literature values depending on the initial pressure and a flatline where potentially the maximum capacity has been reached.

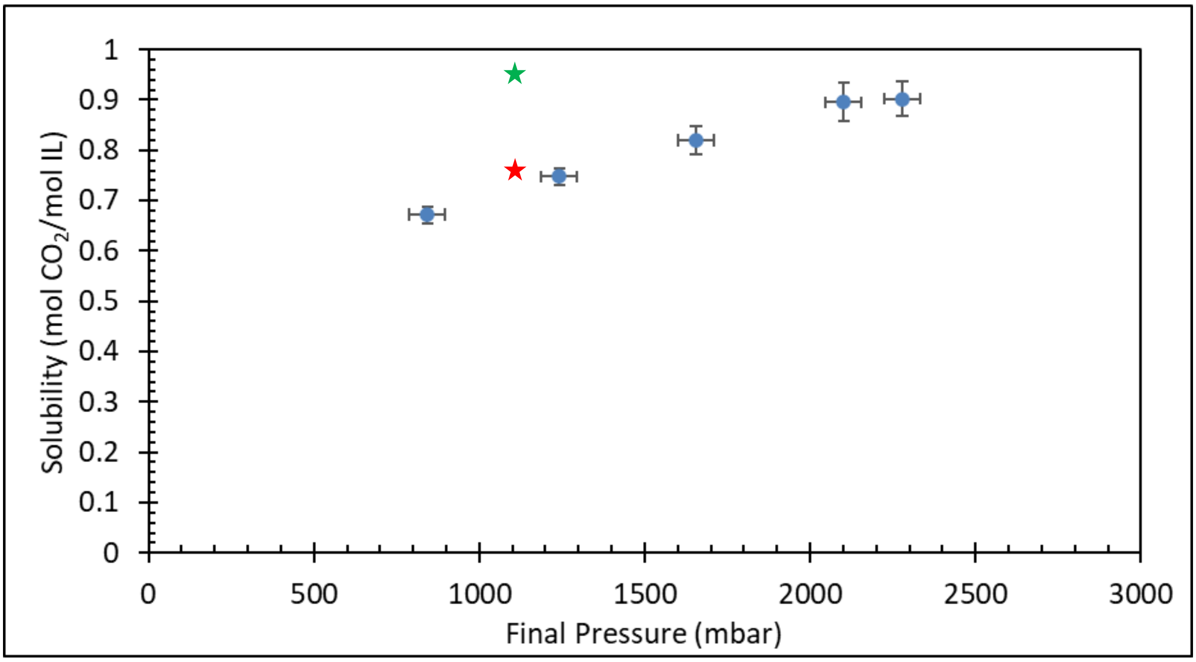


Figure 6 - [DBUH][Im] 35 ^{0}C isotherm (dry IL <0.1 wt% water). 3 vials per data point. Initial pressures of CO_2 from left to right (2000, 2500, 3000, 3500, 4000 mbar). Red star: ref 14 dynamic bubbling experiment at atmospheric pressure. Green star; ref 15 dynamic bubbling experiment at atmospheric pressure, optimised the flow rate to 2L/min waited 3 hours

- DISSOLVE Workshop & Training

Attended the Disordered Materials User Group meeting in Oxford for a week as part of this there was a 3-day DISSOLVE workshop the latest software in analysis of neutron scattering data.

- Database

Database compilation will continue with the focus on chemisorbent ILs making note of the reported anion, cations, capacities, densities, decomposition temperature, water solubility, energy of absorption/desorption. Large variation in anions and cations as papers are added hopefully trends will begin to emerge as the database continues to grow as can be seen in figure 7.

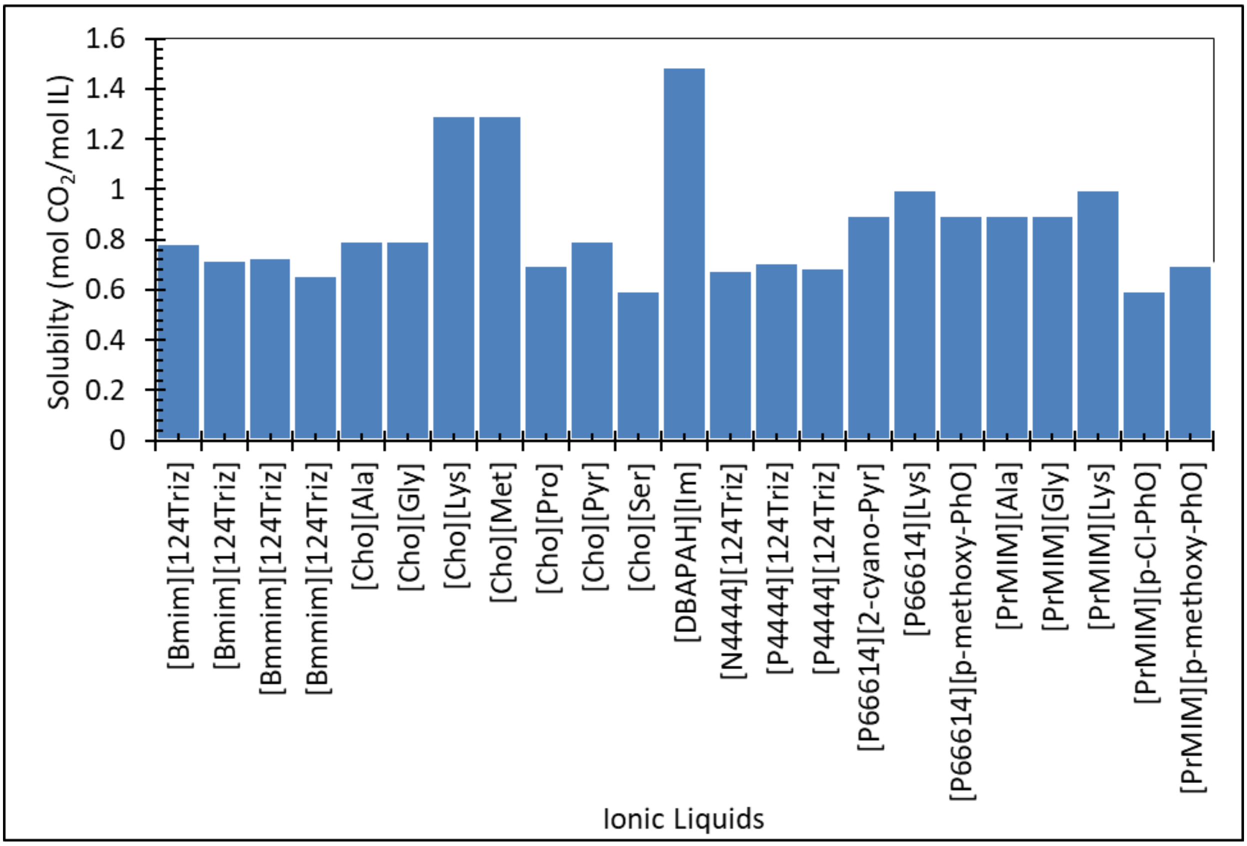


Figure 7 - Extract from database of high CO_2 capacity ILs. ILs from left to right; 1-butyl-3-methylimidazolium-1,2,4,triazolate; 1-butyl-3-methylimidazolium-1,2,4,triazolate; 1-butyl2,3-dimethylimidazolium-1,2,4,triazolate; 1-butyl2,3-dimethylimidazolium-1,2,4,triazolate; cholinium-alanine; cholinium-glycine; cholinium-lysine; cholinium-methionine; cholinium-proline; cholinium-pyrazolate; cholinium-serine; 3-dibutylamino-propylamine-Imidazolate; tetrabutylammonium-1,2,4,triazolate; tetrabutylphosphonium-1,2,4,triazolate; tetrabutylphosphonium-1,2,4,triazolate; trihexyltetradecylphosphonium-2-cyanopyrrolide; trihexyltetradecylphosphonium-lysine; trihexyltetradecylphosphonium-para-methoxy-phenol ; propylmethylimidazolium-alanine; propylmethylimidazolium-glycine; propylmethylimidazolium-lysine; propylmethylimidazolium-para-chloro-phenol ; propylmethylimidazolium-para-methoxy-phenol. Data collected at atmospheric pressure (1 bar) & temperature range of 298-333K.[16–18]

Conclusions and future work

Our results with varying initial pressures of CO_2 yield solubilities that match the previous literature values for ambient temperature for the [DBUH][Im]. Some literature results show that this IL starts presenting significance mass loss at temperatures over 100 ^{0}C.[15] Because this system will be operating at >90 ^{0}C, then this mass loss will be investigated and then solubility will be tested at elevated temperatures starting in May.

The water content in the IL will be varied and CO_2 solubility tested at elevated temperatures along with the regeneration capability and thermal stability. From this we will be able to continue the validate the methodology after benchmarking against ILs from the database and combining the insights gained from the database to design and synthesis new ILs.

References

1. P. Sanglard, O. Vorlet, R. Marti, O. Naef and E. Vanoli, *Chimia (Aarau)*, 2013, **67**, 711.
2. S. A. Ali, A. U. Khan, W. U. Mulk, H. Khan, S. Nasir Shah, A. Zahid, K. Habib, M. U. H. Shah, M. H. D. Othman and S. Rahman, *Energy & Fuels*, 2023, **37**, 15394–15428.
3. X. Wang and C. Song, *Front Energy Res*, 2020, **8**, 560849.
4. M. Pasichnyk, P. Stanovsky, P. Polezhaev, B. Zach, M. Šyc, M. Bobák, J. C. Jansen, M. Přibyl, J. E. Bara, K. Friess, J. Havlica, D. L. Gin, R. D. Noble and P. Izák, *Sep Purif Technol*, 2023, **323**, 124436.
5. X. Li, X. Zhou, J. Wei, Y. Fan, L. Liao and H. Wang, *Sep Purif Technol*, 2021, **265**, 118481.
6. X. Ding, H. Chen, J. Li and T. Zhou, *Carbon Capture Science & Technology*, 2023, **9**, 100136.
7. X. Zhang, X. Zhang, H. Liu, W. Li, M. Xiao, H. Gao and Z. Liang, *Appl Energy*, 2017, **202**, 673–684.
8. M. Perumal, D. Jayaraman and A. Balraj, *Chemosphere*, 2021, **276**, 130159.
9. G. T. Rochelle, *Science (1979)*, 2009, **325**, 1652–1654.
10. Y. Bai, K. Wang, L. Wang, S. Zeng, L. Bai and X. Zhang, *Sep Purif Technol*, 2023, **327**, 124846.
11. B. Lv, B. Guo, Z. Zhou and G. Jing, *Environ Sci Technol*, 2015, **49**, 10728–10735.
12. B. Aghel, S. Janati, S. Wongwises and M. S. Shadloo, *International Journal of Greenhouse Gas Control*, 2022, **119**, 103715.
13. J. M. Young, S. H. McCalmont, S. Fourmentin, P. Manesiotis, J. D. Holbrey and L. Moura, *ACS Sustain Chem Eng*, 2023, **11**, 17787–17796.
14. W. Xiong, M. Shi, L. Peng, X. Zhang, X. Hu and Y. Wu, *Sep Purif Technol*, 2021, **263**, 118417.
15. X. Zhu, M. Song and Y. Xu, *ACS Sustain Chem Eng*, 2017, **5**, 8192–8198.
16. C. Wang, Y. Xie, W. Li, Q. Ren, B. Lv, G. Jing and Z. Zhou, *Chemical Engineering Journal*, 2023, **473**, 145266.
17. P. Sanglard, O. Vorlet, R. Marti, O. Naef and E. Vanoli, *Chimia (Aarau)*, 2013, **67**, 711.
18. X. Hu, X. Yang, L. Chen, M. Mei, Z. Song, Z. Fei, P. J. Dyson and Z. Qi, *Chemical Engineering Journal*, 2022, **435**, 134956.

QUILL Quarterly Report

February– April 2024

Name:	Mark Young		
Supervisor(s):	Dr Leila Moura, Prof John Holbrey & Prof Sophie Fourmentin		
Position:	PhD		
Start date:	October 2020	**Anticipated end date:**	September 2024
Funding body:	EPSRC		

Gas Separation Technologies

I am currently writing my thesis and have completed drafting of two chapters. The plan will be as follows:

Introduction and literature review of low melting mixture for CO_2 uptake.
Gas solubility screening method (published).
TOPO based low melting mixtures for biogas upgrading (drafted).
Nitrile based low melting mixtures for biogas upgrading.
Deuteration of randomly methylated cyclodextrin and its neutron scattering.
Enhancing gas capacity in natural polymers.
Conclusions.

All experimental work is completed, and I hope to finish my thesis by September and viva shortly after.