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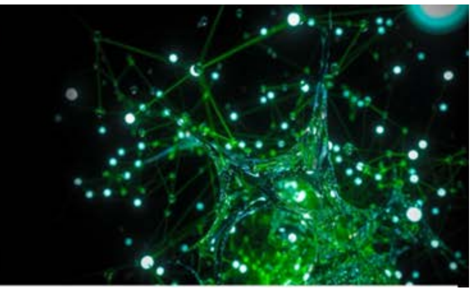


QUILL
Quarterly Reports

August - October 2024

CONFIDENTIAL (up to October 2027)

Contents

QUILL Quarterly Report

August 2024 – October 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 1 and 2 stages 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. The SQUID magnetic analysis process of the synthesized materials continues as planned. I have been informed about the steps such as sample preparation, working principle, and result understanding, and I continue to be informed. The results obtained will be analysed in detail, and the data will be prepared for an academic publication from beginning to end. I still could not achieve a synthesis process that contained boron in the molecular structure. To achieve this, I synthesized new boron-containing ionic liquids. These studies are also continuing.

I presented at QUILL25-MSILDG conference through poster on 2nd of September. I was awarded the best poster prize at the conference. On August 29th, I completed the differentiation meeting, and this step was completed. I have carefully followed the feedback provided by the panel members and am trying to understand and implement their suggestions, especially in thesis writing and academic writing.

In addition to my academic publication goal, I expanded the literature review as a complementary 3rd chapter in my doctoral thesis. Here, I am following research on magnetic ionic liquids in my doctoral thesis. My supervisor, Professor Peter Nockemann, advised me on this subject, and I am following this information. I added the APR plan to the calendar for the end of the year. First, we will focus on this step as a target after publishing our research.

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

August - October 2024

Name:	Aodhán Dugan		
Supervisor(s):	Prof Peter Nockemann, Dr Oana Istrate and Dr Paul 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

In the hunt for ideal deposition of POM particles on GF surface, reduced concentration accompanied by pretreatment of GF and decreased reaction time and temperature supported the growth of nanoparticles. POMu-GF showed no electrochemical improvements in posolyte but improved the performance in negolyte, through improved electrode/electrolyte interaction and increased number of active sites. A flow battery cell was then constructed using POMu-GF as electrode in negative half-cell, the battery performance of which was compared to a flow cell built using heat-treated GF (H-GF) as electrode in both positive and negative half-cell. At a current density of 40 mA/cm^{-2} and flow rate of 50 mL/min, the POMu-GF cell outperformed the H-GF (Figure 1), exhibiting a 4.7% and 3.1% increase in voltage efficiency (VE) and energy efficiency (EE), respectively. Accompanied by a decrease in initial charge potential and increase in initial discharge potential of 0.1 V and 0.09 V respectively, the performance of the battery has been improved across various metrics at this current density. Upon increasing current density to 100 mA/cm^{-2} (Figure 2) the POMu-Gf continued to outperform the H-GF cell, with an increase of 8.4%, 1.8% and 9.2% in VE, CE and EE, respectively along with a decrease in initial charge potential of 0.1 V and increase in initial discharge potential of 0.05 V.

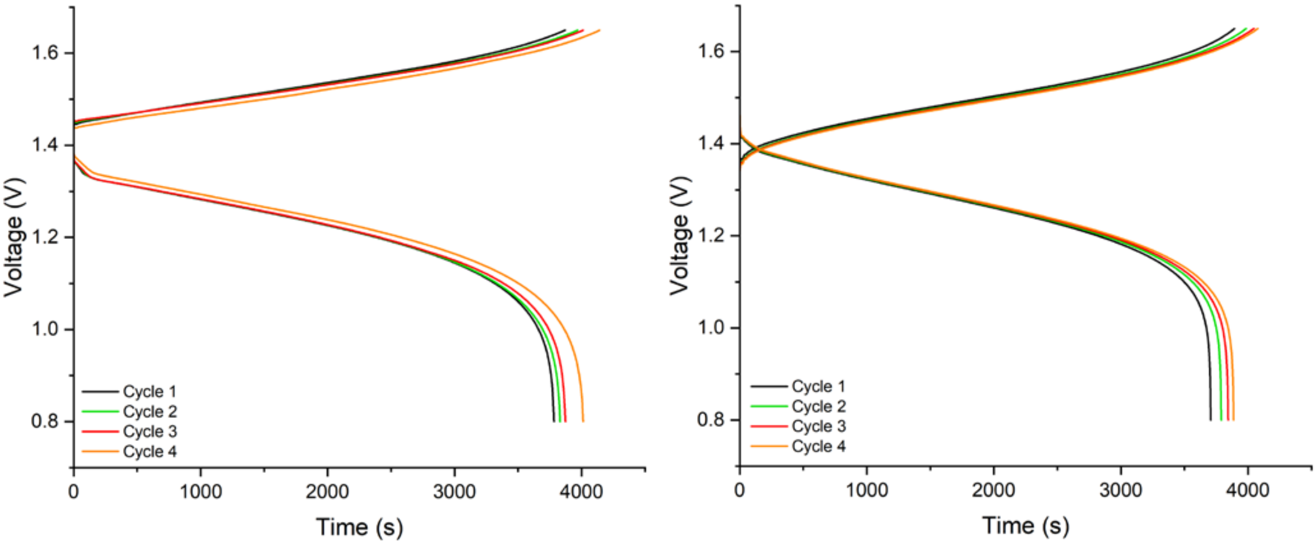


Figure 1 - Charge/Discharge cycles of heat treated (H-GF) and POM treated (POMu-GF) at 40 mA/cm^{-2} with a flow rate of 50 ml/min

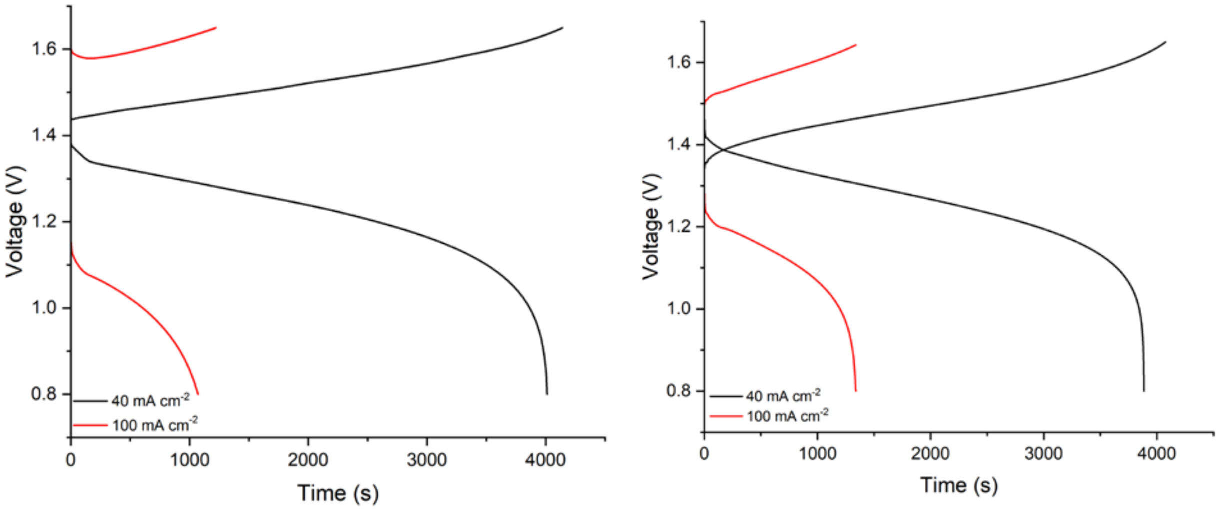


Figure 2 - Charge/Discharge cycles of H-GF and POMu-GF at 100 mA/cm^{-2} with a flow rate of 50 ml/min

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 CV analysis. Upon this improvement in electrochemical performance, full cell testing was conducted in which the POMu-GF outperformed the H-GF in every key metric at both 40 and 100 mA/cm^{-2}. Next steps involve repeat testing across each technique to test repeatability. If all goes according to plan, a research paper detailing the novel use of POMs as electrode modification materials for improved VRFB performance will be produced.

QUILL Quarterly Report

August - October 2024

Name:	Maebh Fitzsimons		
Supervisor(s):	Dr Leila Moura and Professor Stuart James		
Position:	PhD student		
Start date:	01/10/2024	**Anticipated end date:**	01/10/2028
Funding body:	EPSRC & BBSRC		

Sustainable Porous Liquids

Background

Climate change presents an urgent global challenge, primarily fuelled by rising levels of CO_2 emissions from fossil fuels and industrial activities. Effective CO_2 capture and storage technologies are essential to reducing greenhouse gas emissions and limiting global warming. Currently, amine scrubbing is considered the most technologically advanced method for CO_2 capture, relying on chemical reactions between CO_2 and amine solutions. While amine scrubbing is effective and widely used, it has major limitations that make it unsustainable over the long term: it requires significant energy input for regeneration, is highly corrosive, and often involves hazardous by-products that present environmental disposal challenges.

This project aims to create sustainable porous liquids designed for efficient and environmentally friendly CO_2 capture. Unlike traditional solvents, porous liquids combine the fluidity of a liquid with the adsorption properties of a solid, creating a unique medium that can selectively capture CO_2 while reducing many of the drawbacks of amines. Porous liquids provide a more energy-efficient approach to CO_2 capture, as they can reduce the thermal energy needed for regeneration and are non-corrosive, making them safer and more cost-effective for industrial applications.

This work is driven by the principles of green chemistry and green engineering, aiming to develop a technology that is environmentally benign, economically feasible, and inherently safe. Specifically, this project emphasises the design of sustainable materials that minimise waste, energy, and toxic by-products. By replacing conventional amine solutions with porous liquids, the goal is to achieve a scalable, low-impact CO_2 capture method that is aligned with sustainable development objectives.

Ultimately, this research aims to address the critical shortcomings of current CO_2 capture technologies by creating a solution that is both economically and environmentally sustainable. Through innovation in material science and engineering, this project contributes to the larger vision of transitioning industries towards low-carbon practices and achieving global climate goals.

Objective of this work

The project's ultimate goal is to develop sustainable, biobased porous liquids designed for efficient gas capture and separation, providing an affordable solution for retrofitting existing gas purification systems. It aims to create versatile materials with high gas uptake and selectivity, using innovative screening methods to optimise performance across diverse industrial applications

Progress to date

So far, my work has focused on two promising bio-based approaches for developing microporous solids: cyclodextrin metal-organic frameworks (CD-MOFs)[1] and cellulose nanofiber foams[2]. Cyclodextrins offer several advantages, including non-toxicity, high stability, selective adsorption, and a renewable nature. I have begun an investigation into synthesising CD-MOFs[3], aiming to leverage these properties to create high-surface-area materials for gas capture and separation.

In parallel, I am exploring cellulose nanofiber foams, which offer a sustainable, low-cost, and biodegradable alternative. Cellulose foams provide high surface area and mechanical stability, ideal for large-scale applications. Currently, I am conducting a literature review to better understand their synthesis and potential modifications to improve performance.

Most of my initial work has involved background research on these materials to identify key benefits, challenges, and optimal synthesis methods. This foundational knowledge will guide my experimental work as I refine these approaches to create effective, renewable materials for environmental applications.

Conclusions and future work

Moving forward, I will continue my literature review, focusing on advanced characterisation techniques for microporous solids, such as PXRD and BET analysis, to gain deeper insights into their structural and surface properties. In parallel, I will begin synthesising cellulose nanofiber foams to investigate their potential as a sustainable material for gas capture and other environmental applications. The next steps will involve evaluating the activation conditions to ensure the pores of the solids are available for gas uptake, followed by conducting gas capture experiments to assess the material's performance. Specifically, I will use our high-throughput HS-GC method for gas uptake[4], which enables the screening of up to 264 samples per day. In this process, a known amount of sorbent and gas are introduced into vials, and the headspace composition after equilibration is analysed using HS-GC and compared to a calibration. These activities will be crucial for optimising both the synthesis and functionality of the materials for future practical applications.

References

1) Dummert, S. V.; Saini, H.; Hussain, M. Z.; Yadava, K.; Jayaramulu, K.; Casini, A.; Fischer, R. A. Cyclodextrin metal–organic frameworks and derivatives: recent developments and applications. *Chemical Society Reviews* **2022**, *51* (12), 5175-5213, 10.1039/D1CS00550B. DOI: 10.1039/D1CS00550B.
2) Dinesh; Wang, H.; Kim, J. Citric Acid-Crosslinked Highly Porous Cellulose Nanofiber Foam Prepared by an Environment-Friendly and Simple Process. *Global Challenges* **2022**, *6* (11), 2200090. DOI: https://doi.org/10.1002/gch2.202200090.
3) Smaldone, R. A.; Forgan, R. S.; Furukawa, H.; Gassensmith, J. J.; Slawin, A. M. Z.; Yaghi, O. M.; Stoddart, J. F. Metalorganic frameworks from edible natural products. *Angewandte*

Chemie - International Edition **2010**, *49* (46), 8630-8634, Article. DOI: 10.1002/anie.201002343 Scopus.

4) Young, J. M.; McCalmont, S. H.; Fourmentin, S.; Manesiotis, P.; Holbrey, J. D.; Moura, L. A High-Throughput Experimental Approach to Screening Gas Sorption by Liquids and Solids. *ACS Sustainable Chemistry & Engineering* **2023**, *11* (50), 17787-17796. DOI: 10.1021/acssuschemeng.3c05901.

QUILL Quarterly Report

August - October 2024

Name:	Nia Foster		
Supervisor(s):	Dr Paul Kavanagh and 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. 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. We noticed a discrepancy between reported values from different 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. This was the first project carried out.

Objective of this work

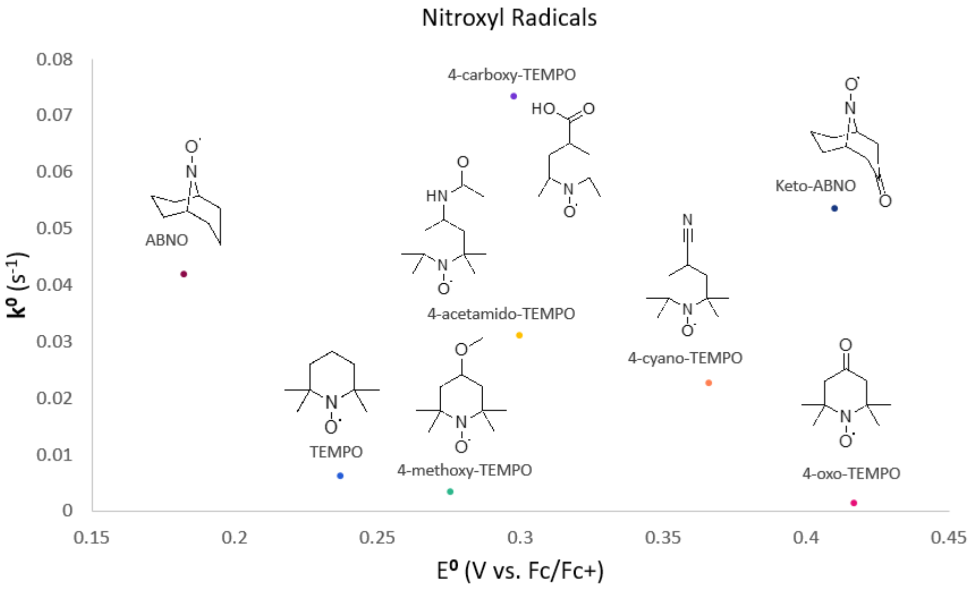
The plan is to study a series of homogeneous redox electrophotocatalysts, specifically reductive electrophotocatalysts. By activating these catalysts though applying a negative potential and exciting them using light, they will have a very high energy that ideally will be used to reduce more difficult 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.

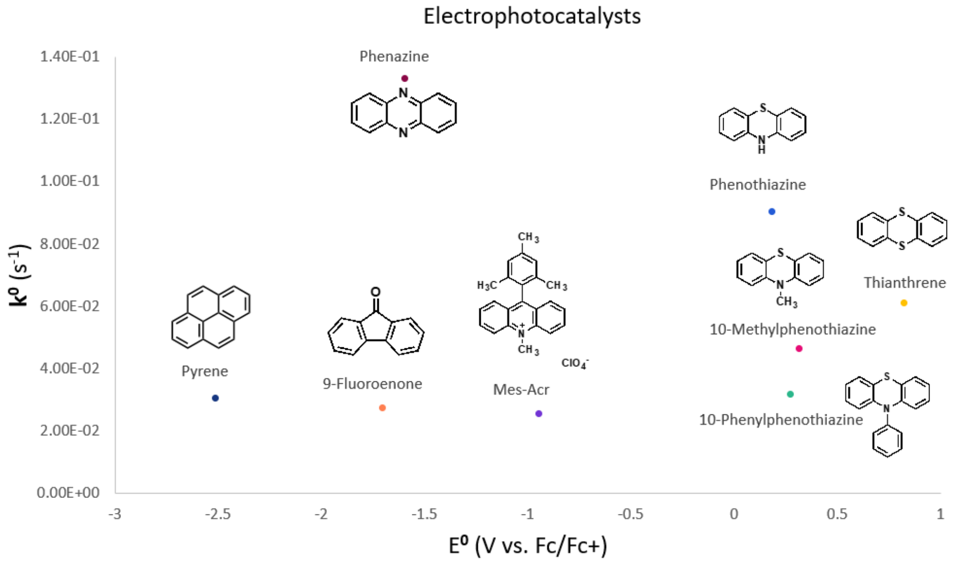
Progress to date

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.

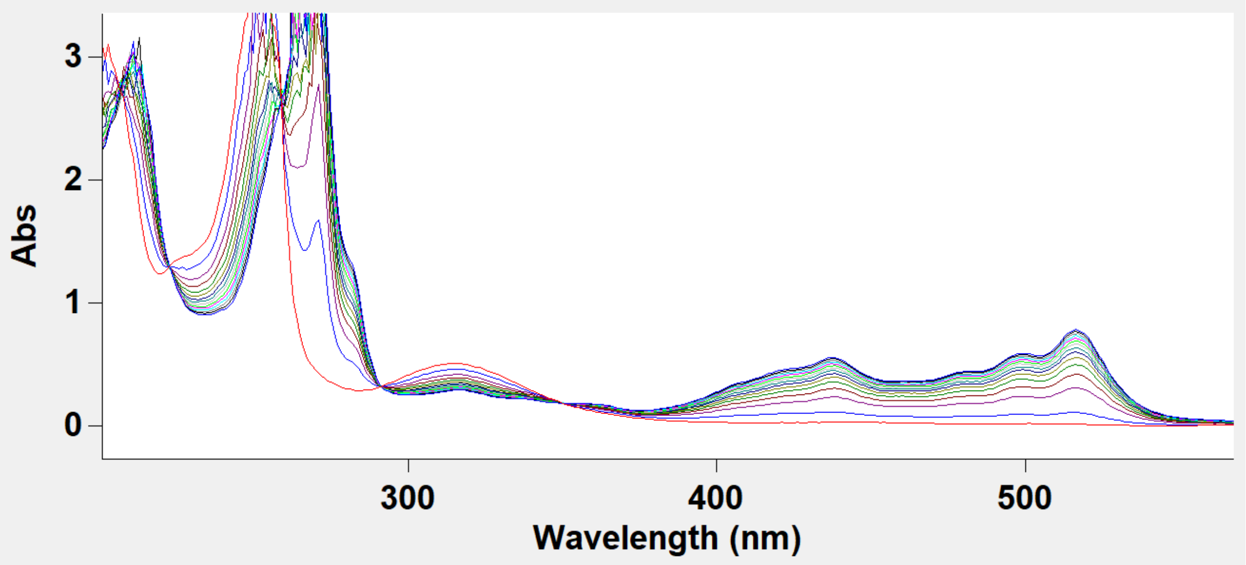
However, we have noticed that there seems to be a lot of disparity between values reported in papers on these parameters, and that they are difficult to reproduce. We believe they are not measured as accurately as they could be, and that alternative methods should be used. Previously, only cyclic voltammetry 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.

Around 50 catalysts have been tested, and graphs such as the ones below have been created for all of them. 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:





Furthermore, preliminary studies have begun on the photochemistry part of the reaction. UV/Vis spectroelectrochemistry has been used, to monitor the change in absorption wavelength of a selection of common electrophotocatalysts as they are being oxidised/reduced. Using these results, we can find the maximum absorption wavelength that will allow us to most efficiently excite the radical ions to be able to further carry out reactions. The data has not yet been analysed but the raw data shows that there is a clear colour change when the catalysts are reduced/oxidised at the electrode, shown below with phenothiazine:



Conclusions and future work

For these electrochemistry results using the RDV, ideally I want to write 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.

I will also be continuing studies on UV/Vis and photocatalysts, possibly probing their excited state lifetimes.

As for the future, we are unsure if the studies on carbon dioxide are still feasible, so studies may continue in a different direction- oxidising alcohols using electrophotochemistry will be the next step.

QUILL Quarterly Report

August - October 2024

Name:	Michael Gamble		
Supervisor(s):	Dr Oana Istrate, Prof Peter Nockemann and 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 active species redox reaction during charge and discharge, they have a major influence on the energy efficiency of the battery at high current densities, which in turn determines required stack sizes and the production costs of the battery. Graphite felt (GF), a type of porous carbon fabric electrode, is commonly employed as the electrodes within a RFB due to its affordability, stability and good conductivity. However, it suffers from poor kinetic reversibility, small specific surface area (< $1 m^2 g^{-1}$), low wettability and limited electrochemical activity with the active species utilized. In response to these issues, a large variety of treatments have been applied to GF by the scientific community. For example, surface treatments, metallic modification, compression variation, non-metal doping and carbonous nanomaterial modification.

A major part of this research will be to assess the ability of protic ionic liquids (PILs) to improve the performance of GF within both an iron and vanadium redox flow battery. 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 optimisation with an iron and vanadium redox flow battery on the performance of the modified graphite felts.

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 and the optimisation of electrode compression.

Progress to date

After the results from the previous quarter, when it was confirmed that carbon could be created on the surface of the fibres of graphite felt, there has been significant progress in determining the ideal mass ratio of choline glycinate ([Ch][Gly]) to graphite felt by conducting a mass ratio study. This involved decorating five samples of heat-treated graphite felt (H-GF) with five different mass ratios of choline glycinate (1:1.5, 1:3.75, 1:5, 1:7.5, 1:15). Furthermore, the presence of nitrogen in the carbon from [Ch][Gly] was confirmed by conducting elemental analysis.

Results from elemental analysis

[Ch][Gly] was pyrolysed at 800 °C for 2 hours under a nitrogen atmosphere and the carbon material that was created is presented in Fig 1. Furthermore, the atom percentages (at.%) of carbon, hydrogen and oxygen calculated after elemental analysis are shown in Table 1.

Figure 1: Image of the carbon material created from the pyrolysis of [Ch][Gly*]*

	Carbon (at.%)	Hydrogen (at.%)	Nitrogen (at.%)
[Ch][Gly] carbon powder	29.32	0.36	5.00

Table 1 - Atom percentages of carbon, hydrogen and nitrogen in the carbon material derived from [Ch][Gly]

Surprisingly, the at.% of carbon is only 29.32% and this is extremely small for the NDC derived from a PIL and suggests that a biochar has been created as similar atom percentages of carbon have been recorded for this class of material. Furthermore, this classification is consistent with the pyrolysis conditions used which are ideal for biochar creation and [Ch][Gly] being composed of two biomolecules. Positively, a nitrogen atom percentage of 5.00 % was observed and this means that the carbon material created is doped with nitrogen and will benefit from the improvements in electrochemical performance yielded from the presence of this element within the carbon structure. The remaining unknown ~65 at.% is likely made up in part by oxygen and the potassium and chlorine from KCl that is created during the [Ch][Gly] synthesis methodology.

Results from mass ratio study

Scanning electron microscope images of untreated graphite felt (U-GF), H-GF and NDC decorated GFs are presented in Fig. 2. The surface of U-GF is very smooth and has negligible structure defects. After thermal activation, visible morphological changes occurred, with an increase in surface roughness, small cavities and incipient delamination all being visible. Only small particles were observed on the fibres of GF-[Ch][Gly]-1.5 (1:1.5 mass ratio), GF-[Ch][Gly]-3.75 (1:3.75 mass ratio) and GF-[Ch][Gly]-5 (1:5 mass ratio). In contrast, GF-[Ch][Gly]-7.5 (1:7.5 mass ratio) was evenly coated with large NDC particles. GF-[Ch][Gly]-15 (1:15 mass ratio) was excessively decorated with NDC that regularly formed large carbon structures between the individual fibres.

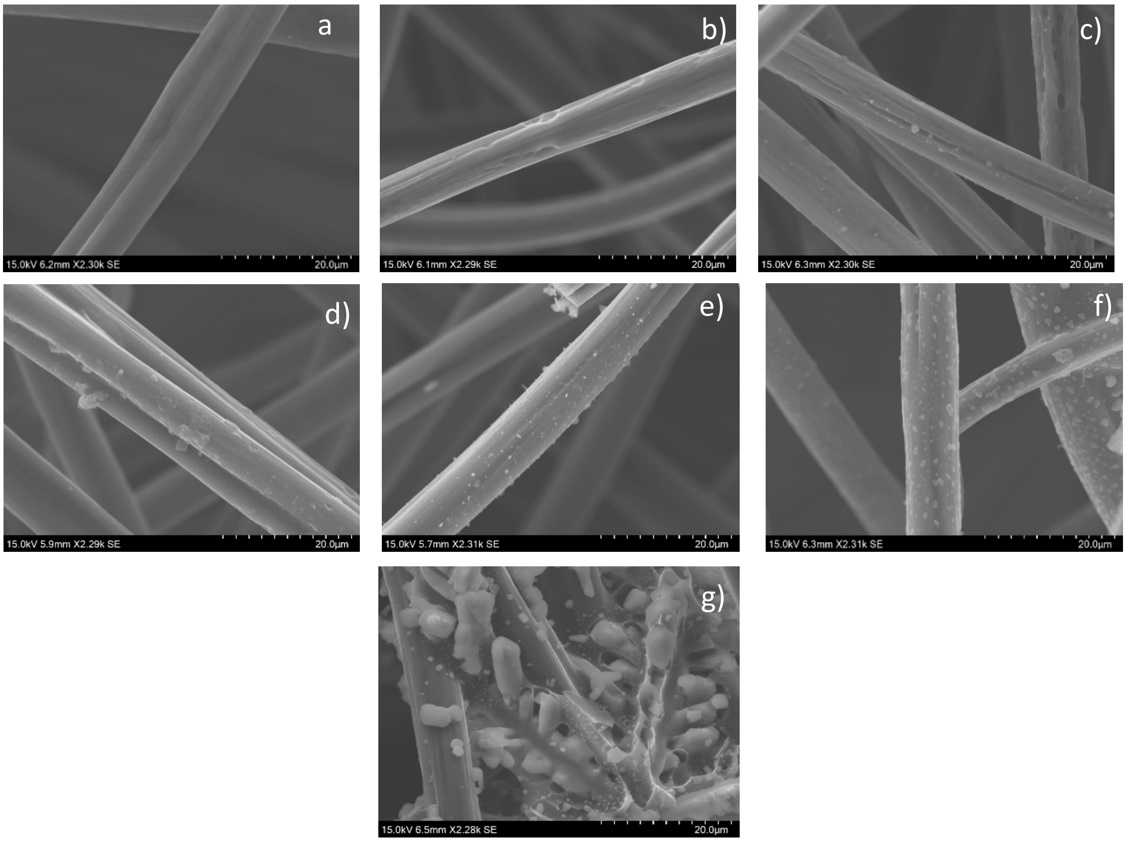


Figure 2 - *SEM SE images of (a) U-GF (b) H-GF, (c)* GF-[Ch][Gly]-1.5, (d) GF-[Ch][Gly]-3.75, (e) GF-[Ch][Gly]-5, (f) GF-[Ch][Gly]-7.5, (g) GF-[Ch][Gly]-15

EDX mapping was used to assess the changing elemental composition on the surface of the fibres of GF and the atom percentages of carbon, nitrogen, oxygen, chlorine and potassium are presented in Table 2. As expected, the vast majority of the felts are composed of carbon (≥85 at.%), owing to their graphitic nature. This is highlighted by untreated GF which has a 99 at.% of carbon. H-GF has more than double the at.% of oxygen compared with U-GF and this is consistent with additional oxygen functionalities added after thermal treatment [12]. The

NDC decorated felts have both potassium and chloride present and this is likely due to the incomplete removal of KCl by-product from [Ch][Gly] synthesis. However, for most of the felts, these elements are present in very small atom percentages (<1 at.%) and do not greatly affect the overall elemental composition of the fibre surfaces. The nitrogen content on the surface of the NDC decorated felts follows an interesting trend. GF-[Ch][Gly]-1.5 has a very high nitrogen at.% of 8.64 and this falls to 3.40 at.% and 0 at.% for GF-[Ch][Gly]-3.75 and GF-[Ch][Gly]-5 respectively. The atom percentage of nitrogen then rises to 7.84 % for GF-[Ch][Gly]-7.5 and 11.67 % for GF-[Ch][Gly]-15. While the changes to nitrogen content require further study, the author believes that the initial decrease may be due to a change from a thin carbonaceous coating covering the surface of the fibres (which has been previously observed whenever NDC derived from an AIL was decorated onto GF in small quantities) to only small individual particles with challenging to detect nitrogen contents being present due to the increasing mass of [Ch][Gly] encouraging individual particle growth. However, this would have to be confirmed using TEM. Progressing the same theory, the rebound in nitrogen content after GF-[Ch][Gly]-5 is because the NDC particles are of sufficient size and surface area where the nitrogen present can be more easily detected by EDX.

Electrode material	**Carbon (at.%)**	**Oxygen (at.%)**	**Nitrogen (at.%)**	**Potassium (at.%)**	**Chlorine (at.%)**
U-GF	99	0.68	0	0	0
H-GF	98	1.64	0	0	0
GF-[Ch][Gly]-1.5	89	1.95	8.64	0.27	0.04
GF-[Ch][Gly]-3.75	91	4.70	3.40	0.18	0.01
GF-[Ch][Gly]-5	97	1.21	0	1	0.23
GF-[Ch][Gly]-7.5	85	0.7	7.84	3.54	3.21
GF-[Ch][Gly]-15	85	1.10	11.67	0.94	0.87

Table 2 - Atom percentages of carbon, oxygen and nitrogen for the different GFs. Outstanding percentages are trace elements

To compare the wettability of the different GFs created, static contact angle testing was conducted with water, catholyte and anolyte. The results attained are presented in Table 3. For both water and the electrolytes, the contact angle with the U-GF was greater than 100 ˚and this confirms the significant hydrophobicity of the material. H-GF has significantly smaller contact angles and this confirms the greater hydrophilicity of this felt because of the introduction of oxygen functionalities via thermal treatment [74]. Whenever the NDC decorated electrodes are studied, the results are consistent with the results of the EDX analysis and the SEM images taken. Initially, NDC decoration significantly improves the wettability of H-GF and only a contact angle of 0 ˚ is observed. This is expected because the NDC will improve the wettability of the electrode by increasing the specific surface area (potentially through the creation of a carbonaceous coating) and by providing hydrophilic nitrogen functional groups. The wettability of GF-[Ch][Gly]-5 almost completely reverts back to that H-GF except for a significantly improved contact angle with water. This is consistent with the recorded 0 at.% of nitrogen and the potential loss of a carbonaceous coating on the surface of the fibres that reduces specific surface area. As expected, GF-[Ch][Gly]-7.5 significantly reverses this trend and GF-[Ch][Gly]-15 returns to the excellent wettability that was observed at lower mass ratios. This likely because there is now sufficiently large NDC particles present to provide the nitrogen content and specific surface area that is equivalent to the coating layer that is possibly is present at lower mass ratios.

Electrode material	**Water (°)**	**Negolyte (°)**	**Posolyte (°)**
U-GF	107	106	123
H-GF	47	72	51.2
GF-[Ch][Gly]-1.5	0	0	0
GF-[Ch][Gly]-3.75	0	0	0
GF-[Ch][Gly]-5	0 (after 3 minutes)	70.15	77
GF-[Ch][Gly]-7.5	0	0 (after 10 mins)	0
GF-[Ch][Gly]-15	0	0	0

Table 3 - Recorded contact angles for water, catholyte and anolyte across the different variations of GF

Cyclic voltammetry was conducted using a three-electrode system in a 50mmol $VOSO_4$ + 2M H_2SO_4 electrolyte to evaluate the electrochemical activity of H-GF and the five different NDC decorated GFs. The preliminary cyclic voltammograms that were created are presented in Fig. 3 and are consistent with the previously attained results. As expected from its excellent wettability, high surface nitrogen content and low coverage of large NDC particles that would create ohmic resistance, GF-[Ch][Gly]-1.5 is the best of the decorated electrodes and signals that NDC decoration can improve electrode performance. This is because the peak potential difference of the decorated electrode is 0.19 V smaller than H-GF which indicates greater electrochemical activity and vanadium redox reaction reversibility. Additionally, the peak oxidation current recorded is more than double that of H-GF which also signifies enhanced activity and reversibility. However, the ratio of the peak currents of oxidation and reduction (which is also a measure of reversibility) for GF-[Ch][Gly]-1.5 is larger than that of H-GF but this could be an anomalous result. After GF-[Ch][Gly]-1.5, the electrochemical performance of the decorated electrodes becomes worse and there is a gradual shift in the shape of the voltammograms created which may indicate a change from the carbonaceous coating to individual NDC particles. For example, from GF-[Ch][Gly]-5, where the shift in the form of NDC decoration is predicted to occur, the oxidation and reduction peaks become more elliptically shaped and more noise is observed.

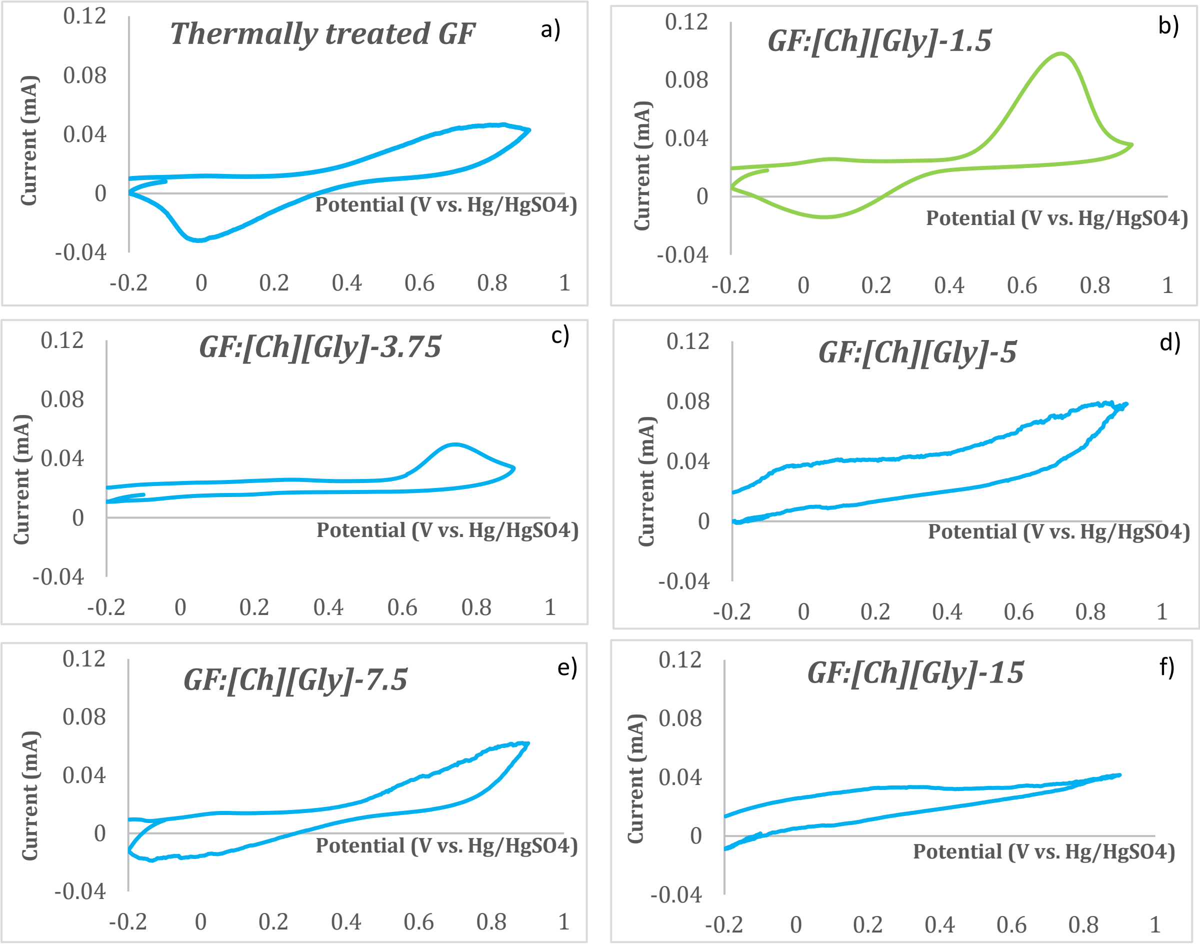


Figure 3 - Cyclic voltammograms of (a) H-GF, (b) GF-[Ch][Gly]-1.5, (c) GF-[Ch][Gly]-3.75, (d) GF-[Ch][Gly]-5, (e) GF-[Ch][Gly]-7.5, (f) GF-[Ch][Gly]-15 in a 0.05M $VOSO_4$ + $2MH_2SO_4$ electrolyte at a scan rate of $10mVs^{-1}$ with a potential window of -0.2V - 0.9V vs. $Hg/HgSO_4$

Conclusions and future work

The mass ratio investigation that has been conducted this quarter is revealing and suggests that [Ch][Gly]-1.5 is the best performing GF. This has been attributed to a potential coating layer that is formed at this mass ratio which provides GF with both a high nitrogen content and a larger specific surface area. However, this will have to be confirmed using TEM. Moreover, the superior electrochemical performance of [Ch][Gly]-1.5 during cyclic voltammetry suggests that a second mass ratio study should be conducted. This is because it is unclear if the ideal mass ratio has been found since most of the other ratios studied are unsuitable and very dissimilar to [Ch][Gly]-1.5. From the elemental analysis of [Ch][Gly] NDC, it has been observed that nitrogen doped biochar has been created due to the very small carbon content (29.3 at.%) of the material. This low carbon content also suggests that there is a large quantity of impurities present that may affect the electrocatalytic performance of the NDC. As a result, once the ideal mass ratio of [Ch][Gly] to GF has been found, it will be important to test if higher pyrolysis temperatures (most likely between 800 °C - 900 °C) can remove a significant proportion of the impurities and enhance the performance of the biochar. Once the ideal mass ratio and pyrolysis temperature have been identified, the next major step would be the completion of vanadium redox flow battery (VRFB) single cell tests to assess improvements to power density that can be attained. Specifically, this will be completed by observing the enhancement to the capacity and EE of the VRFB using the NDC modified electrodes at current densities between 100-300 mAcm^{-2}. After single cell testing using a standard compression ratio, a compression optimisation study will be undertaken to evaluate if further improvements to power density can be achieved.

QUILL Quarterly Report

August – October 2024

Name:	Edwin Harvey		
Supervisor(s):	Dr Oana Istrate, Prof Peter Nockemann and 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.

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.

Since August 2024, I have completed a draft of my first thesis experimental chapter titled: "Tuning Of Latex Concentration for Synthesis of Electrically Conductive Graphene-Poly(Methyl Methacrylate) Nanocomposites". This work focuses on adjusting the PMMA latex/water concentration (e.g., 2.5, 5.0, 7.5 wt.%) and sonicating with expanded graphite. It was found that composites synthesised with a latex concentration of 5 wt.% produced the most electrically conductive compression moulded materials. TGA, Raman, and SEM are used to characterize the presence of graphene in the composites.

My second experimental chapter will focus on the composite's application in redox flow battery electrodes and current collectors. This work characterizes the material using CV, EIS and compression testing. The material is also modified electrochemically by removing the surface polymer resulting in improved electrochemical activity (tested in relation to the V4/V5 couple).

Conclusions and future work

The synthesised composite materials of polymethyl methacrylate (PMMA)/expanded graphite have shown promising electrical and electrochemical properties, as well as being shapeable into cell architectures. Future work includes assembling material into flow fields for testing in zero-gap redox flow cells.

QUILL Quarterly Report

August– October 2024

Name:	Aloisia King		
Supervisor(s):	Prof John Holbrey and 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, a range of 3,5-dicyanopyridinium ILs have been synthesised and fully characterised. These can possibly 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]. 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], C_2CNPyr[NTf_2] and C_3CNPyr[NTf_2] ILs and the mixtures of these ILs with 1-methylnaphthalene. Also, I am currently repeating these measurements so that we can potentially use the data for a publication. I attended the Gordon Research Conference in August and presented our work at it. Finally, we also have a better understanding, potentially of why we were getting lots of side-reactions when we carried out the FLP "proof-of-concept" reactions and have improved our experimental procedure and understand the results and system better.

Conclusions and future work

In terms of the "proof-of-concept" intrinsically IL FLP, we have some repeat experiments to carry out following our improved procedure and provided these results make sense, we potentially have a publication. Additionally, I am finishing the repeat experiments for the EIS measurements of the 4-cyanopyridinium [NTf_2] ILs and the composite mixtures with 1-methylnaphthalene. I plan briefly to carry out conductivity measurements of the other salts that I have made. I am also planning to start writing my thesis.

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

August – October 2024

Name:	Sanskrita Madhukailya		
Supervisor(s):	Prof John Holbrey and Dr Leila Moura		
Position:	Final year PhD student		
Start date:	April 2021	**Anticipated end date:**	April 2025
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 January 2025. As is shown below, the objective and the outcomes of this research work, discussed in the previous quarterly reports, would be explained under 6 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 and 3 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. A section each from this both the chapters is in preparation for a publication, submitted to Prof. John Holbrey, for corrections.

Chapter 4 and 5 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.

Chapter 6 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. 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 7 will include the general summary and conclusion from this thesis work.

Chapter 8 will contain all the spectroscopic data, crystallographic tables, phase diagrams, TGAs, DSCs.

QUILL Quarterly Report

August - October 2024

Name:	David McAreavey		
Supervisor(s):	Dr Stephen Glover, Dr Oana Istrate and 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 modelling of a wide range of thermal runaway events has been successfully completed investigating the use of liquid cooling, PCMs and metallic plates in 2D. As well as this the point of failure of runaway event has also been investigated. The simulations have been further developed to consider a 444 cell module using a partially homogenised array. This allows the behaviour of the full array to be considered with reduced computational requirements.

The main findings to this point are the clear need for indirect liquid cooling to achieve a high standard of thermal management of the cells for the EV application. This means that for the prevention of thermal runaway propagation the system should be based around the use of liquid cooling channels.

The rig designed for the validation of the model has been manufactured, assembled and initial tests along with the associated simulations are being conducted. These tests and simulations are intend to give further conformation of the correct operation of the model.

Conclusions and future work

A wide range of different array attributes have been investigated, the primary focus is now on the validation of the simulation fundamentals against the physical rig. This will constitute several different array designs that should ensure that the simulations have all been constructed in an appropriate way. As well as the refinement of several final designs towards an optimal design using the module level simulation is also under way. This will then allow final 3D simulations to be run that mark the completion of the project.

QUILL Quarterly Report

August - October 2024

Name:	Daniel McCormack		
Supervisor(s):	Prof Peter Nockemann, Dr Oana Istrate and Dr Paul Kavanagh		
Position:	PhD undifferentiated		
Start date:	October 2024	**Anticipated end date:**	October 2027
Funding body:	DfE CAST, and Shell		

Design and Synthesis of Sustainable Electrolytes for Redox Flow Batteries Based on Abundant Metals

Background

The increased use of wind, solar, and other renewable energy sources represents a shift towards a green energy landscape. However, these energy sources are often intermittent and non-dispatchable meaning the development of large-scale energy storage systems is necessary for this shift to be viable. Redox flow batteries (RFBs) are an attractive means of electrochemical energy storage because of their power and capacity can scale independently meaning they can be tailored to the needs of each specific application. They also tend to be safer and more longer lasting then lithium ion batteries and are lower cost per kWh when storing energy for eight hours or more.

Vanadium RFBs have seen commercial application thanks to their high cycle stability and energy efficiency, however they have low energy density and they're widespread use is limited by the rarity and price volatility of the vanadium used as their active materials.

Given this, there is desire for active materials for RFBs based on metals which are more abundant than vanadium. Even metals which do not have the same breadth of available oxidation states as vanadium could still be used when paired with organic ligands which can complex with the metal ions in solution to form complexes with altered redox potentials and activities.

Objective of this work

To design and synthesize new aqueous metal-ligand complexes to serve as the energy storage materials for redox flow batteries that can match or exceed the performance of current commercial vanadium-based electrolytes.

Progress to date

I have read extensively of the current literature on all-iron all-aqueous redox flow batteries and the different iron-ligand complexes that have been used as catholytes and anolytes within them. I have identified the key parameters that are used to evaluate the utility of an active material, namely solubility, redox potential, optimum pH, diffusion coefficient and activity coefficient, exchange current density and membrane permeability. I have also identified the key parameters for a full flow cell: open circuit voltage, discharge capacity, capacity degradation rate, energy efficiency and peak power density.

I have begun my lab work by making up nine solutions of Fe(BIS-TRIS) complex with varying metal: ligand: base molar ratios. BIS-TRIS is a promising electrolyte for forming the negative iron redox couple but the nature of its bonding to iron ions in aqueous solution is not well understood and the ideal electrolyte formulation is yet to be conferment.

Planned Research

I plan to run CV scans of the various formulations of Fe(BIS-TRIS) solution I have made to determine which gives the best reversibility in the redox reactions. I shall also take the UV-vis absorbance of each of the nine solutions to determine in which the iron complex is most soluble and take the ionic conductivity and pH of each solution.

Next, I shall investigate the properties of the permanganate redox couple as a catholyte material that can be paired with an iron-based negative negolyte, when compared to the widely used hexacyanoferrate redox couple. I shall take CVs, UV-vis absorption, ionic conductivity of each redox couple and measure their stability to repeated charge-discharge cycles by CV.

Next, I intend to synthesize EDTS, a tetra sulfonated ligand which forms highly stable iron anolyte complexes and investigate its redox properties. Provided these experiments go well I will be able to construct a full cell test using permanganate and Fe(EDTS).

QUILL Quarterly Report

August – October 2024

Name:	Emma McCrea		
Supervisor(s):	Prof Małgorzata Swadzba-Kwasny and 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.

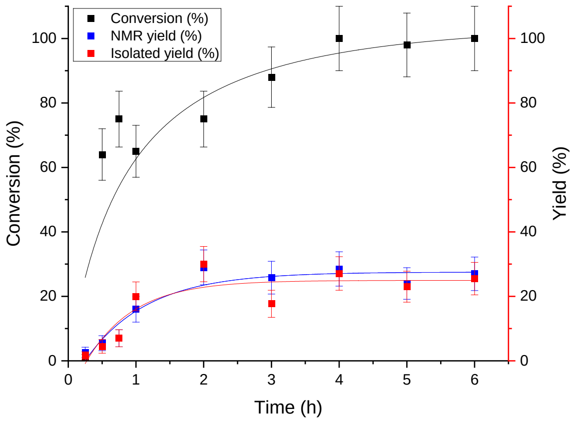
Objective of this work

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 depolymerization at 100°C revealed that higher temperatures and increased catalyst loading were necessary to achieve optimal results. The reactions were conducted using two different solvents, ionic liquid and methanol, which produced distinct outcomes. Using ionic liquid as the solvent presented challenges in isolating a pure product from the reaction mixture, leading to reduced yields due to the ionic liquid's retention of the product. Conversely, methanol, acting as both a solvent and reactant, facilitated product isolation by causing it to precipitate upon cooling, significantly improving the separation and yield.

During the separation process, water proved unsuitable for removing the product, as it hydrolysed it into undesired terephthalic acid (TPA). Instead, a combination of hot and cold methanol was employed to successfully recrystallize the product and separate unreacted PET and ionic liquid. A range of reactions at varying temperatures and compositions has since been conducted to optimize the process. This effort has refined both the separation and analytical techniques, allowing for more efficient analysis of the reaction products.



Conclusions and future work

Currently, efforts are focused on writing a research paper for submission in February, with experimental work expected to conclude in January. The synthesis of boron-based ionic liquids is also underway to support future studies. Once the current phase is complete, research will shift toward investigating the recycling of polyurethanes using ionic liquids, aiming to develop effective methods for their chemical recovery.

QUILL Quarterly Report

August – October 2024

Name:	Kerri McKeever		
Supervisor(s):	Prof Gosia Swadzba-Kwasny and 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

In August, I made d6-dimethyl sulfate which was to help Aloisia with her beamtime at ISIS in September, looking at Frustrated Lewis pairs, the synthesis involved using chlorosulfonic acid and deuterated methanol. Additionally, I started to prepare things for the other beamtime at ISIS in September that I was doing which was looking at Urea and $AlCl_3$ Liquid coordination complexes, this involved drying the urea and performing freeze-thaw on the toluene solvents in order to introduce them into the glovebox.

Additionally, I also spent this month preparing for the QUILL meeting which was held in September, where I presented a poster. During this month, I had meeting with coworkers at Diamond with whom we are continuing the work on the x-ray work which we collected in January and in 2023, we talked about the paper which we hope to complete soon, this is about the x-ray Raman spectroscopy and x-ray absorption spectroscopy analysis we completed on a set of boron Lewis acids in order to develop a new scale of Lewis acidity.

Additionally in this quarter I applied for additional beamtime at the ESRF, ISIS and Diamond which, if approved, should be taking place next year at some point.

I spent September also preparing the $AlCl_3$-urea LCC samples for the ISIS beamtime which I attended at the end of the month and in October as well as helping out with Aloisia's beamtime.

In October, I then started to prepare samples for another ISIS beamtime in December, which is studying FLP on a solid support. I have started to synthesis ^{11}B-BCF and deuterated ionic liquids, along with the help of Aloisi Pete and Yoan with the other parts for these complicated samples.

To prepare ^{11}B-BCF, I first need to make ^{11}B-trimethyl borate from ^{11}B-boric acid and methanol, which was quite tricky to isolate the product as it forms an azeotrope with methanol, and it was complicated to separate this azeotrope, which I did by doing a fractional distillation followed by freezing the azeotrope in a dry ice/acetonitrile bath and then adding concentrated sulfuric acid which separates into two layers and the top is neat trimethyl borate.

Additionally in October, I completed glovebox training by MBraun, we learned a lot about how to operate the box and how to regenerate it and purge it and the systems and protocols in place to use it.

Conclusions and future work

During this quarter, I carried out a lot of synthesis for a number of different beamtimes, including Aloisia's FLPs, the ALCl3-urea LCCs and my FLP beamtime. I attended the QUILL meeting where I presented a poster and continued to work on the X-ray work.

Going forward, I will be continuing synthesis of these sampled for ISIS in December and then completing synthesis for Diamond beamtime in January, after that I will be conducting data analysis from all of these beamtimes and continuing to complete the x-ray paper

QUILL Quarterly Report

August - October 2024

Name:	Erin McKinley		
Supervisor(s):	Dr Oana Istrate and Prof Peter Nockemann		
Position:	PhD Student		
Start date:	October 2024	**Anticipated end date:**	October 2027
Funding body:	EPSRC/Ionic Technologies		

Ionic Liquid Additives for Improved NdFeB Recycling from End-of-Life Magnets

Background

The demand for rare earth elements is continuously growing due to the increase in green and sustainable technologies. These elements have unique physicochemical properties which makes them essential in applications such as wind turbines and electric vehicles. The mining of the rare earths from their ores is not sustainable due to the large amounts of energy required and the limited availability of the primary sources. China is the main supplier of rare earth elements, however as demand increases, other countries cannot rely solely on exportation of these elements to meet their needs. Therefore, producing the rare earths from secondary sources (such as end of life NdFeB magnets) is a more sustainable approach. Solvent extraction is one of the main methods used to recycle end of life magnets, which involves an extraction, scrubbing and stripping step. This process has proven to be effective in separating the 'light' rare earth elements from the 'heavy' rare earth elements using traditional extractants. However, there is difficulty in separating adjacent rare earths due to their similarity in ionic radius, ionic charge and coordination environment.

Objective of this work

This project is in partnership with Ionic Technologies, and the goal is to improve the NdFeB magnet recycling process, specifically improving the separation of the adjacent light rare earths, neodymium and praseodymium. The aim is to find an extraction system that provides high extraction efficiency and high selectivity which could potentially be used commercially in a solvent extraction process. There are some environmental issues associated with the use of traditional extractants in solvent extraction, however ionic liquids are a possible alternative with fewer environmental implications. Therefore, this project will involve incorporating ionic liquid additives into synergistic extractant systems.

Progress to date

So far, a series of benchmark experiments are being conducted to gather initial data on the extraction behaviour of two commonly used extractants (P507 and D2EHPA) through shake out tests followed by analyse using ICP-OES. These tests will quantify the effects of extractant concentration, organic to aqueous solution ratio and degree of saponification on the extraction of Nd from an Nd/Pr feed solution. Following on from this the effect of adding ionic liquid additives to the extractant system will be explored. ICP-OES and NMR analysis will be used to investigate the mechanism of the extraction reactions which will direct the course of future work.

Conclusions and future work

Future work will focus on screening different ionic liquid additives to devise a novel synergistic extraction system. Particularly, functionalised ionic liquids which could be tailored to specific organic extractant systems. Non-ionic liquid additives will also be explored. The precise direction of future work will be data-led, based on experiment and literature, however mathematical modelling work will also be used to supplement the understanding required to uncover a commercially viable extractant system.

QUILL Quarterly Report

August - October 2024

Name:	Shannon McLaughlin		
Supervisor(s):	Professor Gosia Swadźba-*Kwaśny*		
Position:	PhD Student (4th year)		
Start date:	October 2020	**Anticipated end date:**	January 2025
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 January 2025

QUILL Quarterly Report

August – October 2024

Name:	Beth Murray		
Supervisor(s):	Prof Małgorzata Swadźba-Kwaśny and Prof John Holbrey		
Position:	PhD		
Start date:	October 2022	**Anticipated end date:**	December 2025
Funding body:	Department of Economy		

Inorganic Chemistry of Group 13 Elements in Sustainable Uses

Background

Since returning from my three-month break from PhD studies (carrying out research project with Ionic Technologies from July-October), I have been extending the research I carried out at Monash University in Melbourne. This work is on 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]

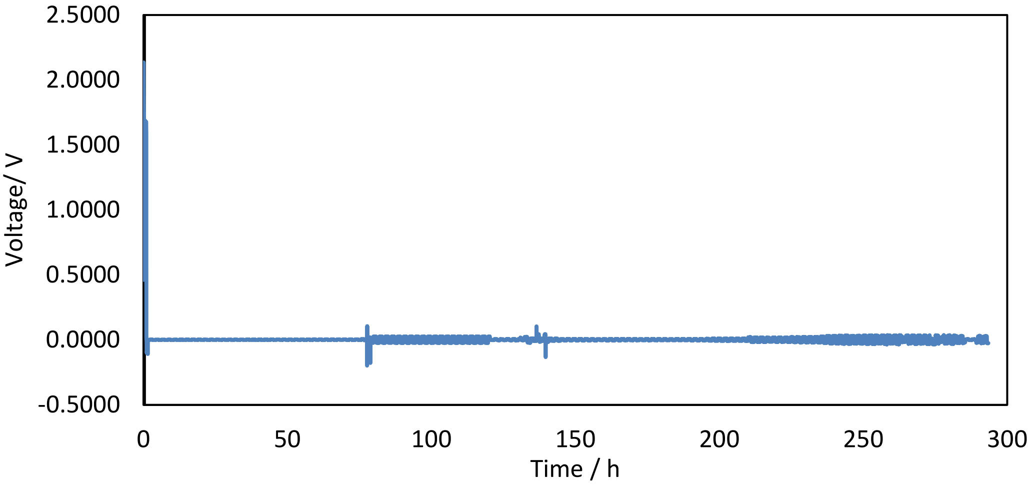


Figure 1 - Galvanostatic cycling of Al/Al symmetrical cell with urea-$AlCl_3$ electrolyte

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).

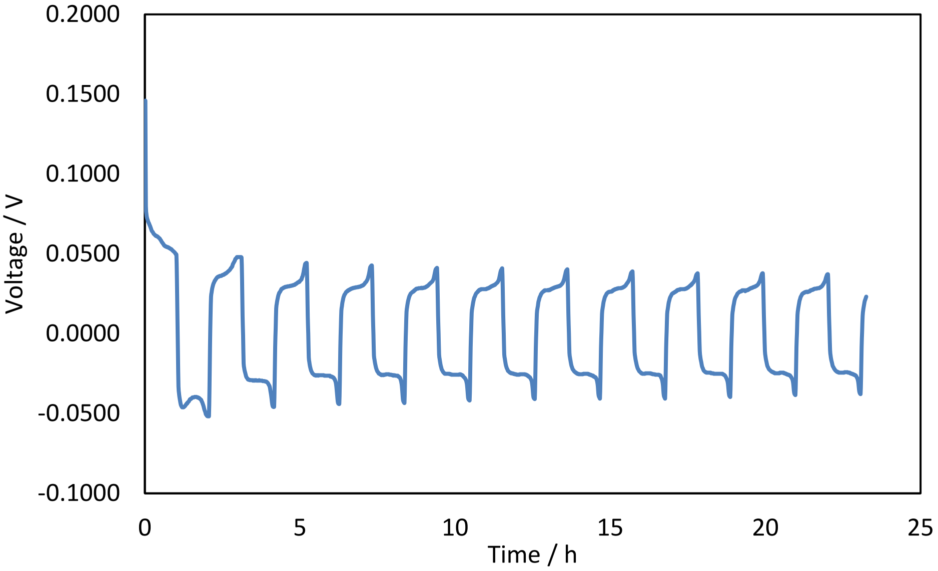


Figure 2 - Galvanostatic cycling of Al/Al symmetrical cell with urea-$AlCl_3$ electrolyte, after the Al electrodes were polished with acid

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).

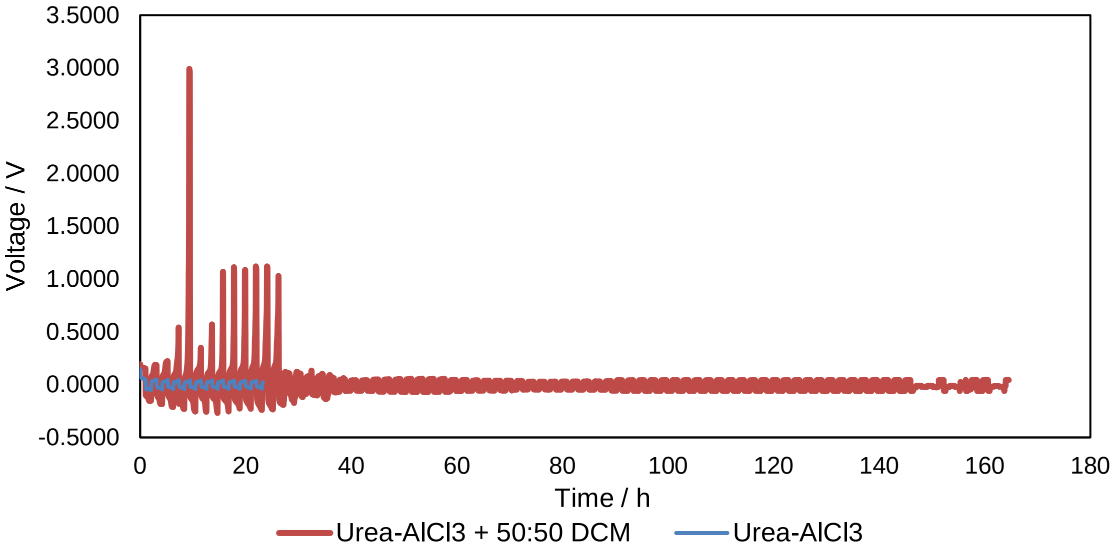


Figure 3 - Comparison of symmetrical Al/Al cycling with urea-$AlCl_3$ electrolyte and urea-$AlCl_3$ electrolyte with the addition of equimolar amounts of DCM

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.

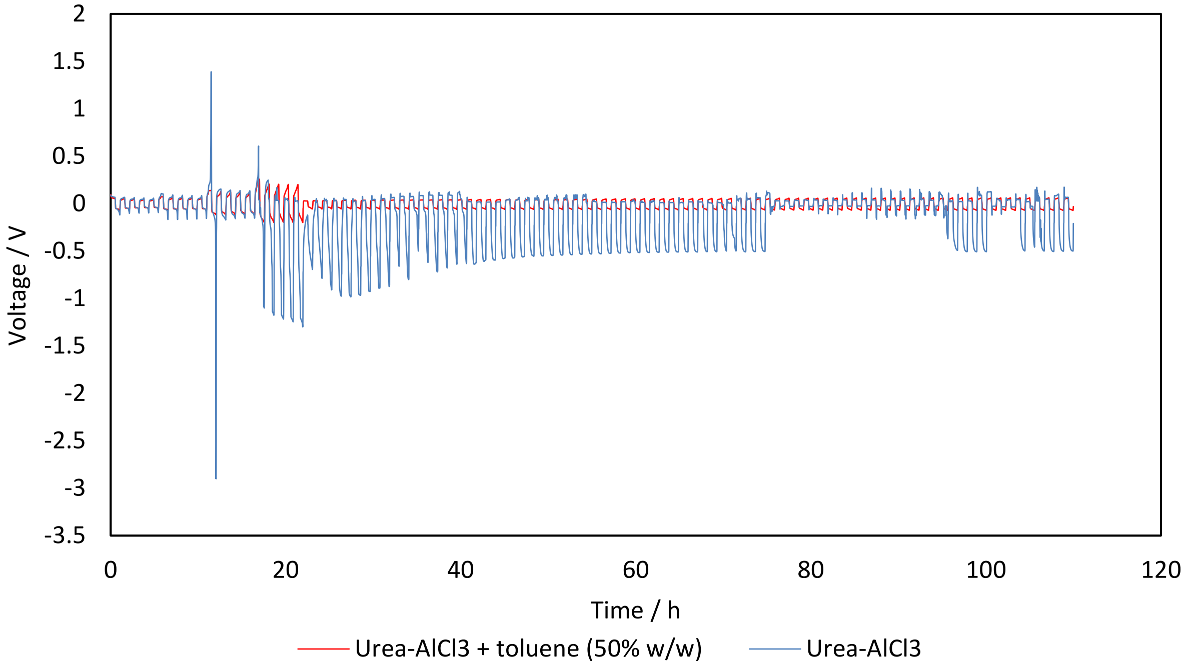


Figure 4 - Comparison of symmetrical Al/Al cycling with urea-$AlCl_3$ electrolyte and urea-$AlCl_3$ with the addition of toluene (50% w/w)

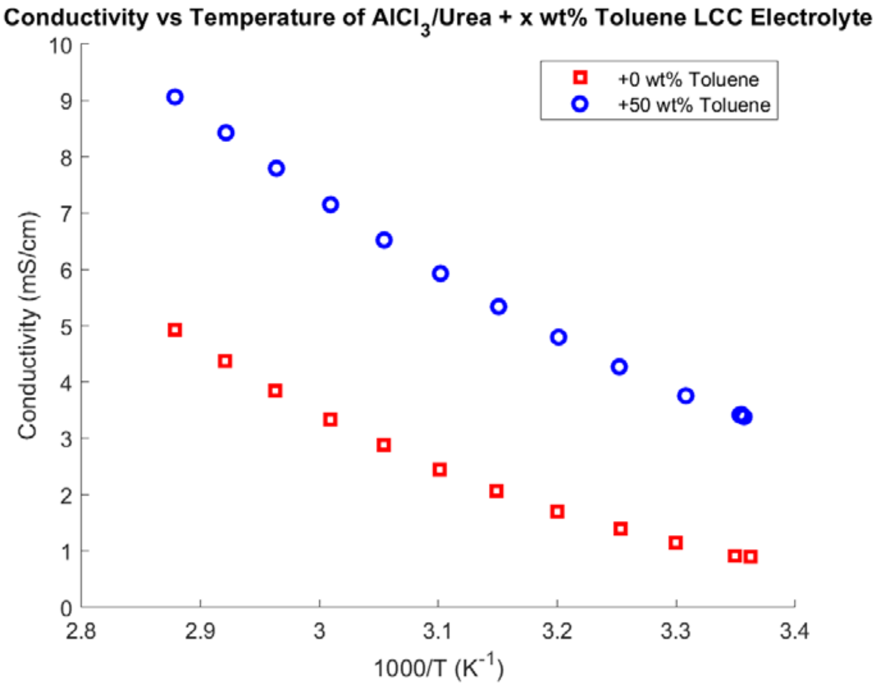
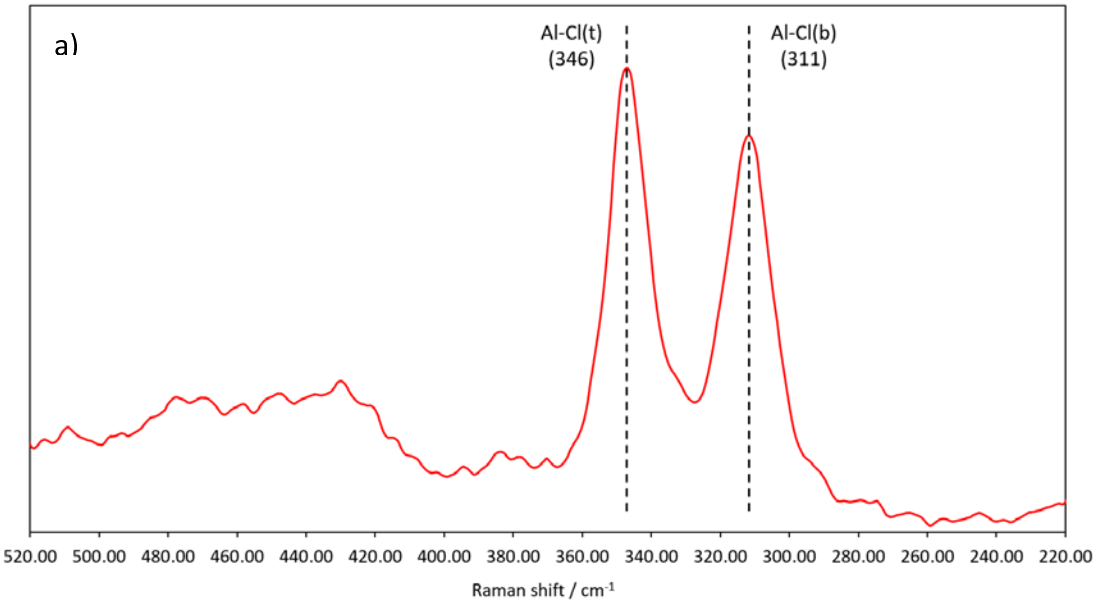


***Figure 5** - Conductivity of urea-$AlCl_3$ + wt% toluene*

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).



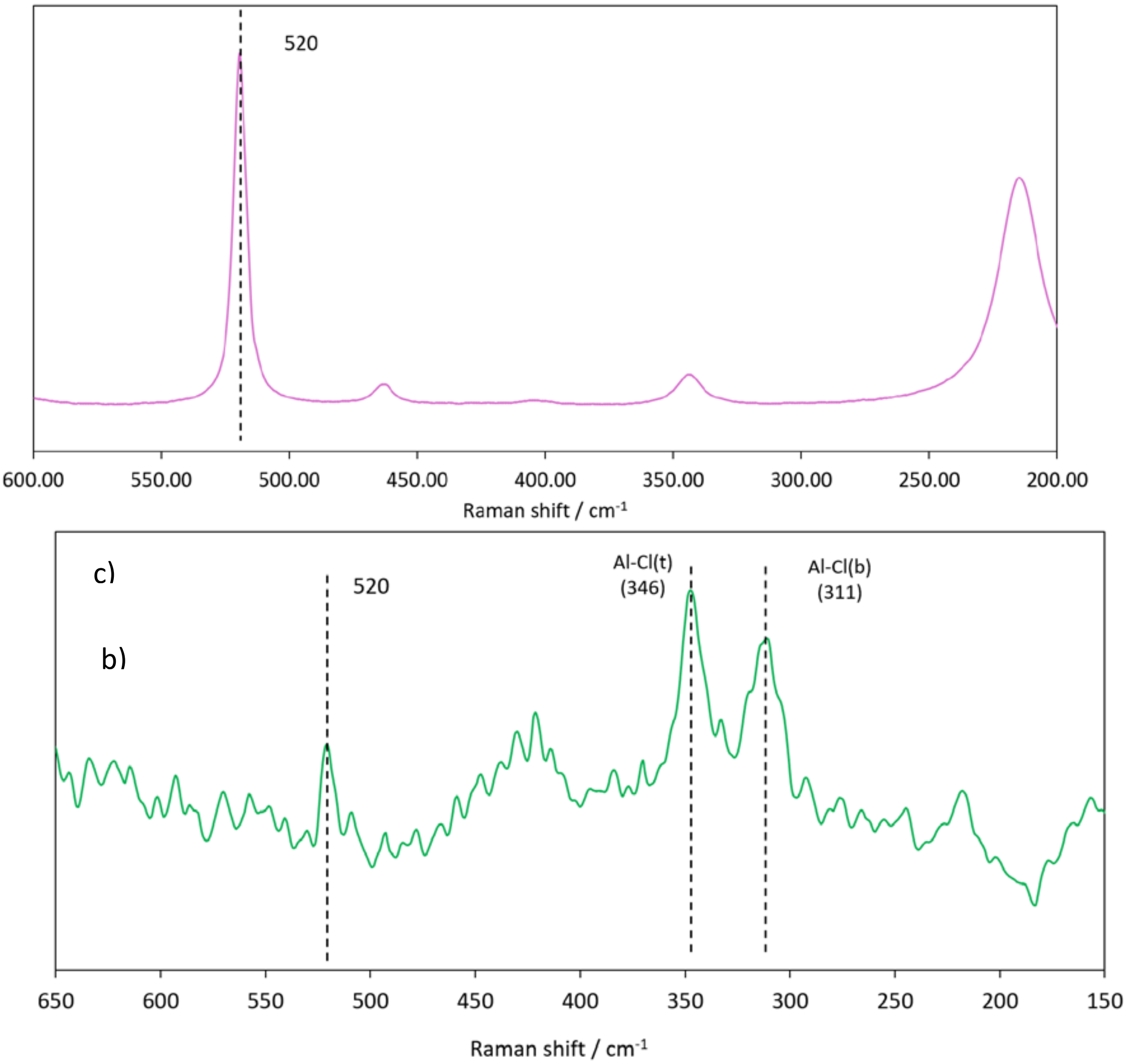


Figure 6 - Raman spectra of a) pure LCC, b) pure toluene and c) LCC + 25% toluene

Figure 7 shows the ^1H 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.

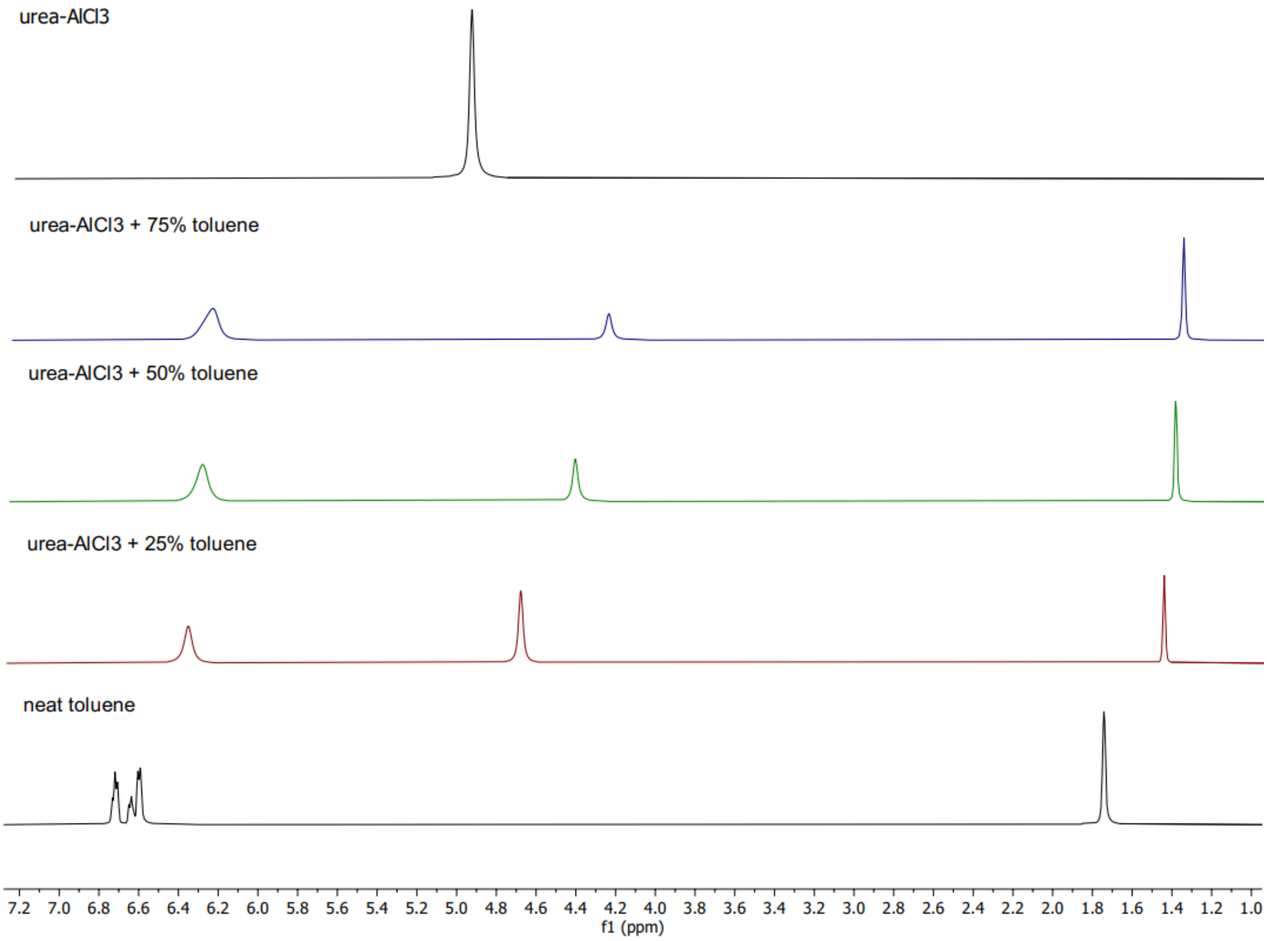


Figure 7 - ^{1}H NMR comparison of urea-$AlCl_3$ with toluene (25%, 50% and 75%) with neat urea-$AlCl_3$ and neat toluene. NMR solvent: d_6-DMSO (capillary).

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.

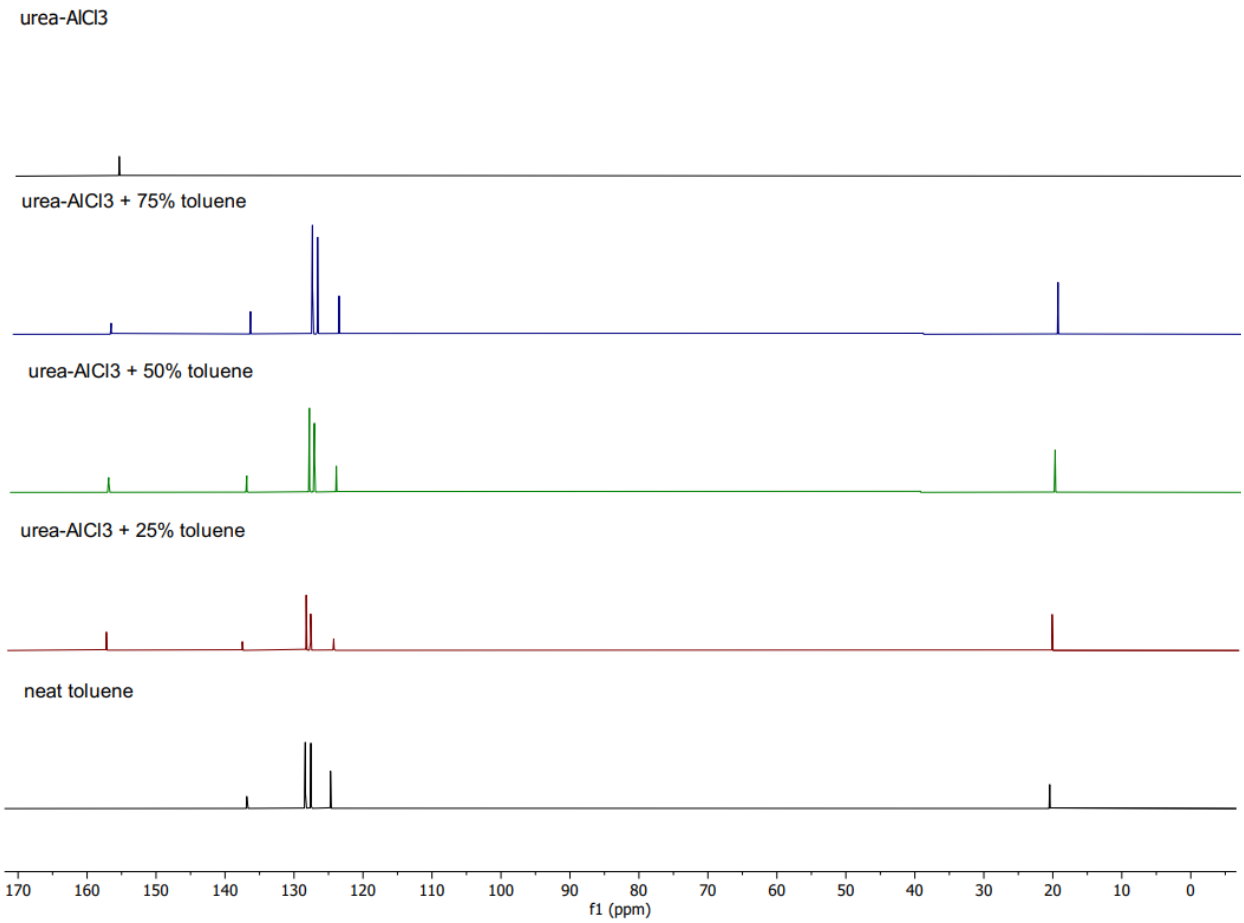


Figure 8 - ^{13}C NMR comparison of urea-$AlCl_3$ with toluene (25%, 50% and 75%) with neat urea-$AlCl_3$ and neat toluene. NMR solvent: d_6-DMSO (capillary)

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.

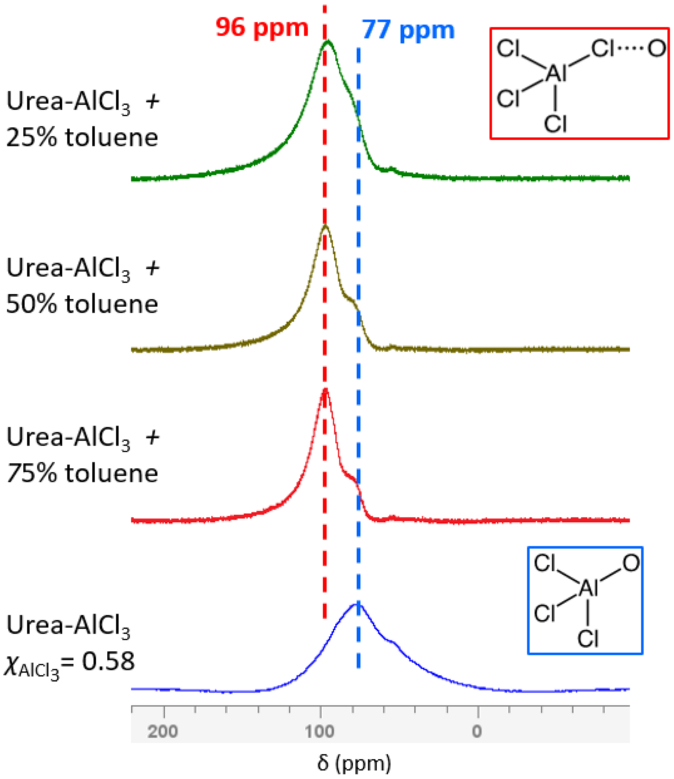


Figure 9 - ^{27}Al NMR comparison of urea-$AlCl_3$ with toluene (25%, 50% and 75%) with neat urea-$AlCl_3$ and neat toluene. NMR solvent: d_6-DMSO (capillary)

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.

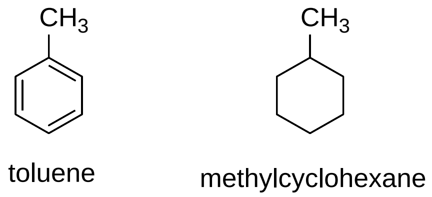


Figure 10 - Chemical structures of toluene and methylcyclohexane

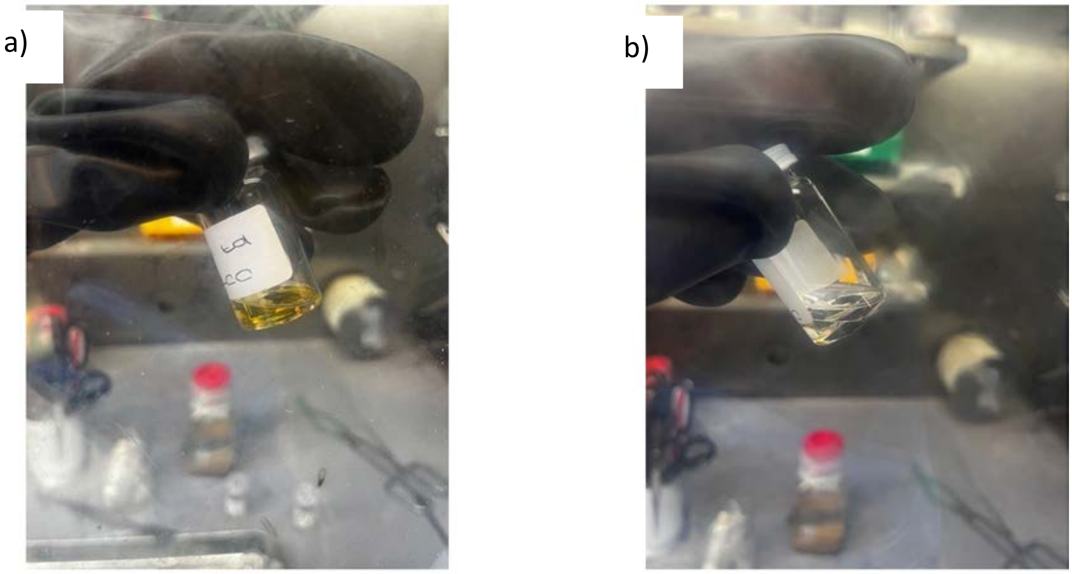


Figure 11 - a) toluene mixed with LCC to form one layer and b) methylcyclohexane mixed with LCC to form two layers

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

I also carried out work at ISIS Neutron and Muon source in October, to obtain neutron scattering data on this work. The aim is to gain a deep understanding of the speciation of the electrolyte with and without toluene. The experiments were successfully carried out and the data is being analysed/modelled, to allow the interactions between the different atoms to be understood.

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.

Over the next few months, further work will be carried out with the aim of submitting for publication in January 2025. Work that needs to be completed before publication includes obtaining cleaner Raman spectra, as well as putting together the rest of the paper in collaboration with our colleagues in Australia.

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, 1 edn., 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. C. Ferrara, V. Dall’Asta, V. Berbenni, E. Quartarone and P. Mustarelli, *The Journal of Physical Chemistry C*, 2017, **121**, 26607-26614.
16. M. Angell, G. Zhu, M.-C. Lin, Y. Rong and H. Dai, *Adv. Funct. Mater.*, 2020, **30**, 1901928.
17. A. Bakkar and V. Neubert, *Electrochim. Acta*, 2013, **103**, 211-218.

QUILL Quarterly Report

August – October 2024

Name:	Junzhe Quan		
Supervisor(s):	Prof John Holbrey and Dr Leila Moura		
Position:	PhD		
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 Water Treatment, Desalination and Separation

List of Chapters:
Chapter1: Literature Review
Chapter2: Building a new method to measuring cloud points of ionic liquid (IL)-water system by using Crystal16
Chapter3: Setting up the Lab-scale Forward Osmosis test system and benchmark
Chapter4: Using lab-scale FO test machine to test tetrabutylphosphonium 5-phenyltetrazolate solution as draw solute both under FO and PRO modes
Chapter5: COSMO-therm simulation and modeled economic cost in industry
Chapter6: Conclusion and Future work

Expected Submission Date:
March 2025

QUILL Quarterly Report

August - October 2024

Name:	Pranav Sharda		
Supervisor(s):	Dr Josh Bailey		
Position:	PhD student		
Start date:	1st October 2024	**Anticipated end date:**	1st Oct 2027
Funding body:	EPSRC		

Implementing Ionic Liquids in PEM Fuel Cells

Background

Increased use of renewable energy sources, such as wind or solar, is vital to prevent climate disaster. However, these sources of energy are intermittent (for example, sunlight is only available in the daytime) and non-dispatchable (cannot be shipped). This necessitates an increase in global energy storage capacity of *ca*. 1000 GWh by 2030 (BloombergNEF). To address seasonal fluctuations in supply and demand of energy, the world is turning to green hydrogen as a potential solution. The most efficient way to convert hydrogen back to electricity is by using a fuel cell, which generates voltage from the separate reactions of hydrogen and oxygen, giving water as the by-product. The most common fuel cell type is the polymer electrolyte fuel cell (PEFC) that uses platinum electrocatalysts and hydrated perfluorinated membranes. However, their commercial adoption is limited by the high cost of these materials and the low tolerance of today's PEFCs to fuel impurities. Recently, alternative materials, using ionic liquids as components of membranes and catalyst layers, have shown promising results that may unlock greater uptake of this important electrochemical technology.

Objective of this work

1) To produce a range of composite membranes (ionomers) from judiciously selected protic ionic liquids and poly(ionic liquids), and characterise their chemical, mechanical, and electrochemical properties.
2) To explore methods for the combination of these ionomers with Pt and non-Pt electrocatalysts and apply electrochemical techniques to probe their viability for use in fuel cells.
3) To produce a membrane-electrode assembly from the most promising candidates for single-cell laboratory testing.

Progress to date

1) Began literature review on PEMFCs and the typical materials and methods of fabrication used for anhydrous intermediate temperature PEMFC.
2) Identified *in-situ* polymerisation as an underutilised method of fabrication for polymer electrolyte membranes, I intend to apply this technique to known pairs of ionic liquids and polymers to check if there is a difference in properties compared to conventional solution casting.

3) Ordered, set up, and tested gas-sealed rotating disk electrode cell, will be conducting cyclic voltammetry experiments using this equipment initially to benchmark the conventionally used materials for PEMFC.
4) Ordered the following equipment for single-cell fuel cell testing:

    a. Temperature controller and thermocouple
    b. Cartridge heaters
    c. Mass flow meters
    d. Insulation jacket

QUILL Quarterly Report

August – October 2024

Name:	Michael Sweeney		
Supervisor(s):	Dr Leila Moura and 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 $^{\circ C}$ to release the CO_2.[9] Couple this with the mass loss at the operating temperatures, it's a system fit for redesign.

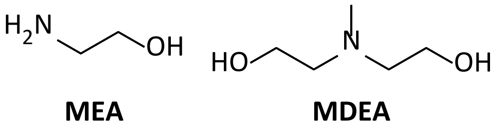


Figure 12 - Structure of common amines used in CO_2 scrubbing

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.

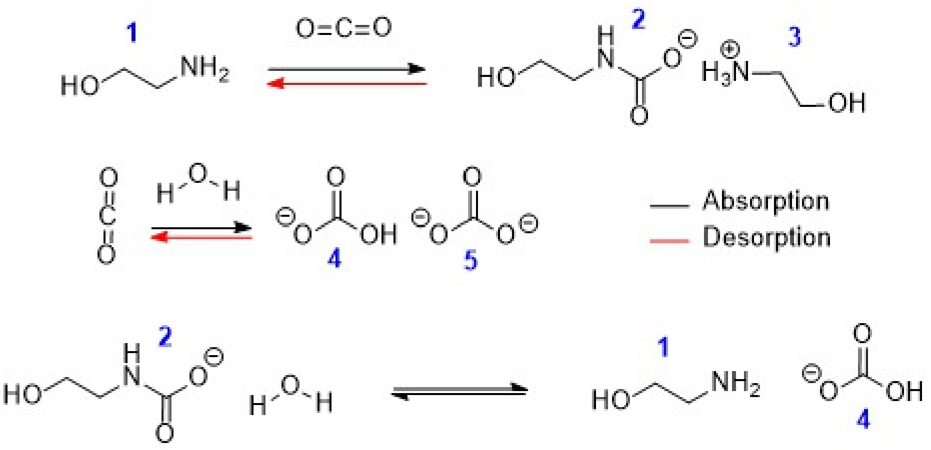


Figure 13 - Reaction pathway for MEA & CO_2

Due to issues with amine scrubbers outlined above a replacement is needed. A range of protic and aprotic ILs were synthesis for assessment of A) thermal stability and B) CO_2 uptake capacity. Huang et al.[11] showed the succinimide anion has a high CO_2 uptake capacity. Increasing the electron donating effect of the backbone and thusly the basicity of the anion may increase CO_2 uptake. Fang et al.[12] calculated the basicity of the succinimde based anions using B3LYP/6-31++G(p,d).

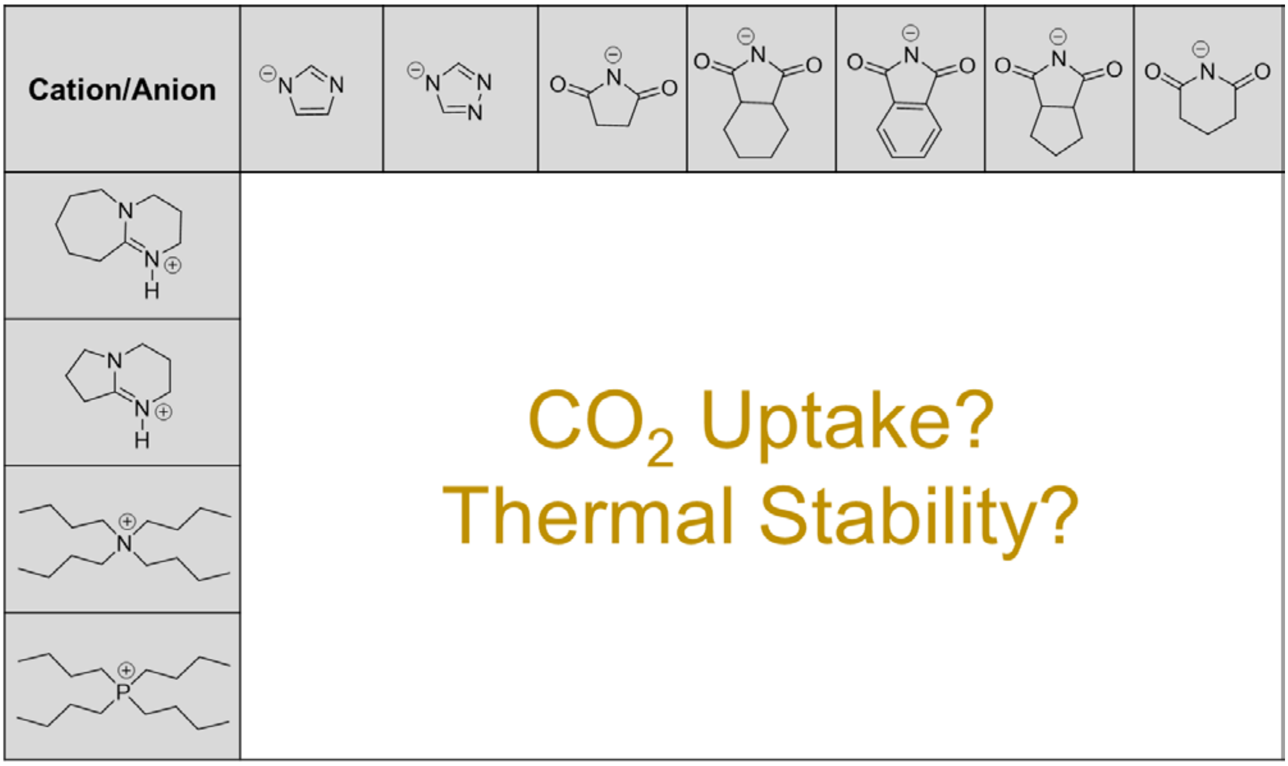


Figure 14 - Matrix of protic and aprotic ILs. Cations (top to bottom); 1,8-diazabicyclo(5.4.0)undec-7-enium ($[DBUH]^+$), 1,5-diazabicyclo[4.3.0]non-5-enium ($[DBNH]^+$), tetrabutylphosphonium ($[P_{4444}]^+$) and tetrabutylammonium ($[N_{4444}]^+$). Anions (left to right);

imidazolide ([Im]$^-$), 1,2,4-triazolide ([Triz]$^-$), succinimide ([Suc]$^-$), 1,2-cyclohexanedicarboximide ([CyhexSuc]$^-$), phthalimide ([Phth]$^-$), 1,2-cyclopentanedicarboximide ([CypentSuc]$^-$), glutarimide ([Glut]$^-$)

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 alternative under investigation are 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 CO_2 scrubbing. In Figure 4. the thermal stability of some of the ILs have been highlighted.

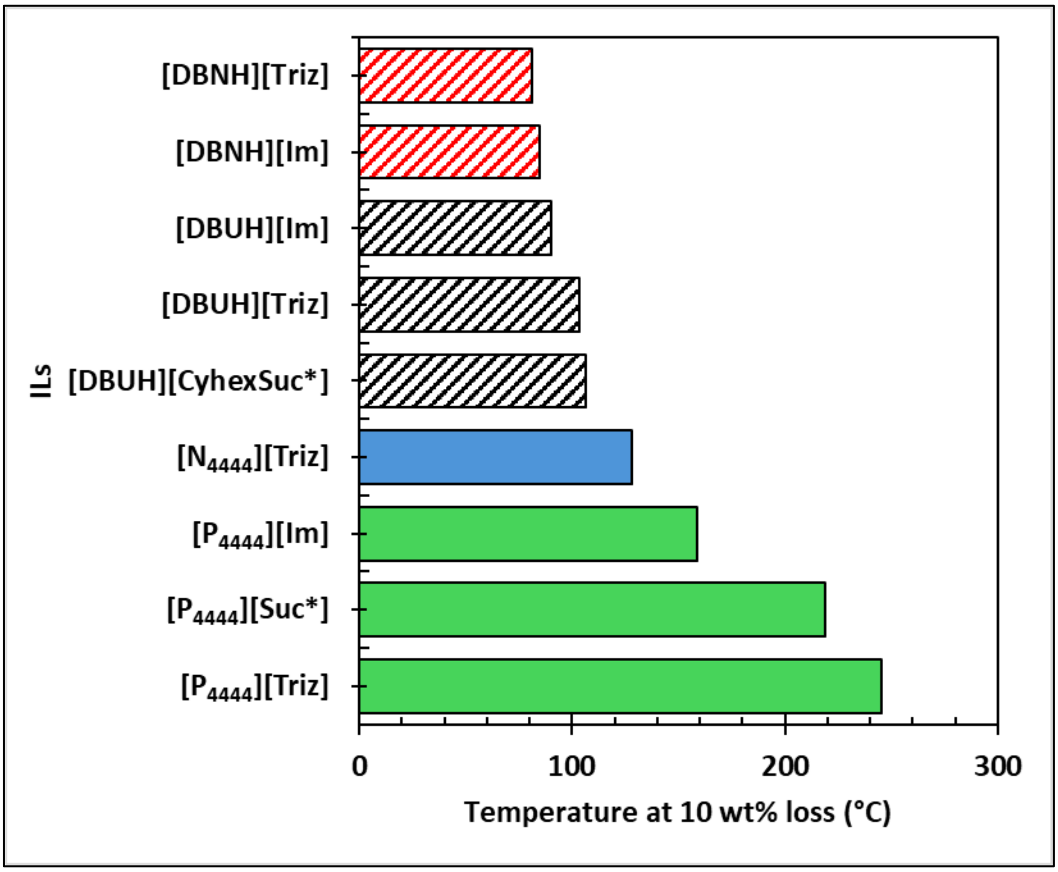


Figure 15 - TGA analysis using sealed aluminium pans with a heating rate of 1 K /3 min. Temperature taken when the sample had reached 10 wt% mass loss. Dashed bars; protic ILs. Full coloured bars; aprotic ILs. Red dashed bars, [DBUH] based ILs. Black dashed bars; [DBUH] based ILs. Blue bar [N_{4444}] based ILs. Green bars; [P_{4444}] based ILs.

A clear trend appears between the protic (dashed bars) and the aprotic (full bars) ILs showing aprotic ILs > protic ILs in regard to thermal stability. This can be contributed to the inherently volatility of the protic ILs as there is an equilibrium of the acid-base neutralisation reaction that exists between the starting materials and the IL. This equilibrium can be shifted in favour of the IL formation by increasing the ΔpK$_a$ between the cation precursor and the anion precursor. However aprotic ILs are not in equilibrium with the starting materials and as such offer a negligible vapour pressure and high thermal stability as can clearly be seen in Figure 4.

CO$_2$ Solubility in Protic ILs

The protic ILs, [DBUH][Im], [DBUH][Triz], [DBUH][Im], [DBNH][Triz] were tested for CO2 uptake using the HS-GC screening method as outlined previously.[13] Following the determination of the optimal equilibration time (21 hours and 74 hours for [DBUH][Im] and [DBUH][Triz] respectively) the HS-GC measurements took place after these times can elapsed. For [DBNH]+ based ILs HS-GC screening took place after a week as no equilibration time experiment was conducted.

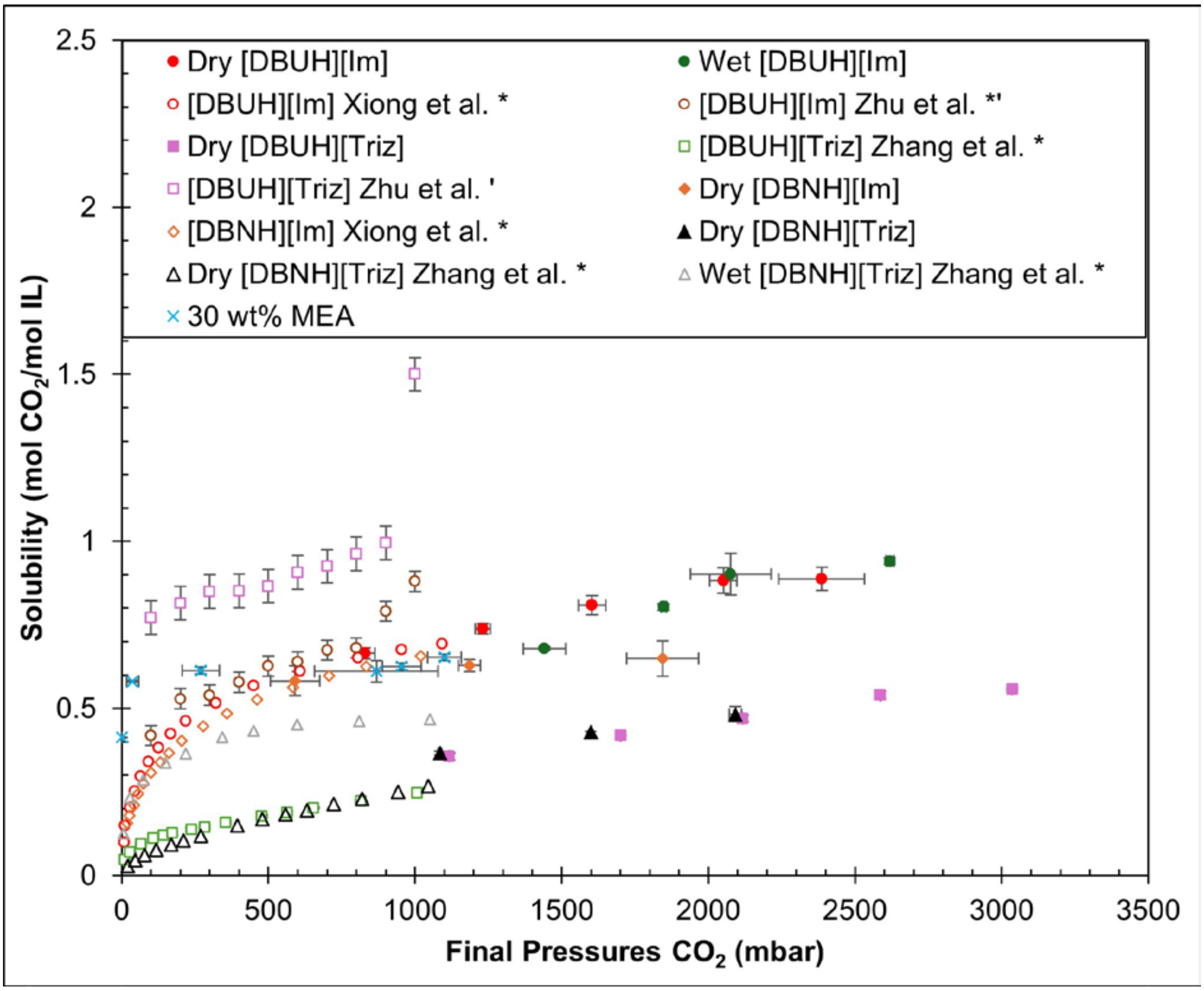


Figure 5 - CO$_2$ uptake in ILs at 35 °C in a static uptake system unless otherwise stated. * = uptake at 40 °C. ′ = dynamic uptake system. Filled symbols are this work, unfilled symbols are from the literature. Red circle; 0.33 g of dry [DBUH][Im] (>0.1 wt% water). Green circle; 0.37 g wet [DBUH][Im] (14 wt% water). Red circle outline; [DBUH][Im] Xiong et al.[14] Brown circle outline; [DBUH][Im] Zhu et al.[15] Pink square; 0.2 g of dry [DBUH][Triz] (>0.1 wt% water). Green square outline; [DBUH][Triz] Zhang et al.[16] Pink square outline; [DBUH][Triz]

Zhu et al.[17] Orange diamond; 0.27 g of dry [DBNH][Im] (>0.1 wt% water). Orange diamond outline; [DBNH][Im] Xiong et al.[14] Black triangle; 0.28 g of dry [DBNH][Triz] (>0.1 wt% water). Grey triangle outline; wet [DBNH][Triz] (3.5 wt% water) Zhang et al.[16] Blue cross; 1 g of 30 wt% MEA in water, Young et al.[13]

The CO_2 uptake values from this work along with the reported literature values can be seen in Figure 5 with the solubilities plotted against the equilibrium pressure deduced from the HS-GC screening method. 30 wt% MEA is also included as a benchmark to the industrial standard. From our results we can determine the order of CO_2 uptake to be [DBUH][Im]>[DBNH][Im]>[DBUH][Triz] >[DBNH][Triz] in terms of mol CO_2/mol IL. As is evident from the graph, ILs that employ the imidazolide anion have a higher CO_2 uptake capacity than those that are triazolide based. This can be rationalized using ΔpK_a as imidazole is a weaker acid than triazole therefore imidazole has a more nucleophilic conjugate base leading to enhanced CO_2 capture. Saturation of the [DBUH][Im] seemed to have been achieved meaning that the chemisorption part of the CO_2 uptake has been reached stoichiometrically which can be seen for both the dry and the wet [DBUH][Im] with the flat-lining of CO_2 uptake at $\approx$ 0.9 mol CO_2/mol IL (Figure 6 red circles, green circles) which is higher than the industrial standard, 30 wt% MEA aqueous solution which has a saturated capacity of 0.6 mol CO_2/mol IL (Figure 6 blue triangle outline). For low partial pressure the reported literature values for [DBUH][Im] match however deviate at pressures over 800 mbar. This can be down to the experimental set up different between the static system and the dynamic bubbling system, in the static system the CO_2 is the limiting factor whereas in the dynamic system the CO_2 is in continuous supply. Aprotic ILs are scheduled to be tested for the CO_2 uptake now.

Conclusions and future work

Aprotic ILs have shown enhanced thermal stability over protic ILs which experience the onset of mass loss at around 90 °C, similar to amine scrubbers the current industrial scrubber. Succinimide anion is susceptible to hydrolysis and ring opening when using the hydroxide cation precursor.[18,19] We are currently working on an alternative synthesis route to prevent the hydrolysis. Completion of the IL matrix shown in Figure 2 will continue. An experimental set up is being established to determine the vapour pressure of the protic ILs. CO_2 uptake for the aprotic ILs using a screening method and absorption/desorption of CO_2 will be assessed and a potential goldilocks zone established with the basicity of the anion to desorption.

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. Y. Huang, G. Cui, H. Wang, Z. Li and J. Wang, *Journal of CO2 Utilization*, 2018, **28**, 299–305.
12. W. Fang, F. Xu, Y. Zhang, H. Wang, Z. Zhang, Z. Yang, W. Wang, H. He and Y. Luo, *Catal Sci Technol*, 2022, **12**, 1756–1765.
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. X. Zhang, W. Xiong, L. Peng, Y. Wu and X. Hu, *AIChE Journal*, 2020, **66**, 1–11.
17. X. Zhu, M. Song, B. Ling, S. Wang and X. Luo, *J Solution Chem*, 2020, **49**, 257–271.
18. Y. Huang, G. Cui, Y. Zhao, H. Wang, Z. Li, S. Dai and J. Wang, *Angewandte Chemie International Edition*, 2019, **58**, 386–389.
19. M. Zanatta, N. M. Simon, F. P. dos Santos, M. C. Corvo, E. J. Cabrita and J. Dupont, *Angewandte Chemie International Edition*, 2019, **58**, 382–385.

QUILL Quarterly Report

August - October 2024

Name:	Malka Urooj		
Supervisor(s):	Prof John Holbery		
Position:	PhD Student		
Start date:	1st October 2024	**Anticipated end date:**	12th May 2028
Funding body:	Self-funded		

Synthesis and Applications of Borates

Background

Ionic liquids (ILs) are composed of ions and exist in liquid state at temperatures below 100°C. Ionic liquids incorporating boron-based anions of interest in terms of (i) expanding the scope and portfolio of available non-fluorous anions available and (ii) to include the benefits of their elemental composition within a variety of applications including battery and capacitor electrolytes and SEIs. Discovery of borates anions is considered as viable alternative expanding the scope of ILs. Since 1990's studies have shown the importance of borates ILs and have evolved significantly from the initial discovery. The tetrafluoroborate anion, $[BF_4]^-$, was the first borate anion incorporated into ILs with good thermal stability and resistance to chemical degradation. The electrochemical properties of ILs with borates exhibit wide electrochemical properties which is potential significant for batteries. The anions of borates show very strong ionic interactions with good conductive properties. Advances in uses of non-fluorinated borate anions within ILs for electrochemical applications, to-date, have been driven by O/O-chelated orthoborate anions s such as *bis*(oxalate)borate ($[BOB]^-$)

Objective of this work

The main focus of this study is to synthesize new N/O- and O/O chelated borate anions for incorporation into both organic and solvate ILs, taking advantage of the potential for cost effective and easy synthesis to build-in direct pathways for scale-up for applications from the start of the program. to design non-toxic ionic liquids that can used in energy storage devices and for gas capture and transformation. The scalable synthesis process will be with continuous flow methods for large scale production. At this point (for the APR that will come at the start of the new year) the objectives with borate anions are to explore the potential to use N/O- and N/N-chelating ligands to form orthoborate anions that can be studied as components of conventional ionic liquids (i.e. combined with organic cations such as tetraalkylphosphonium or methylbutylpyrrolidinium etc) and also their application as sodium (or other metal salts) as solvate-ILs when combined with small amounts of solvents.

The overall approach will include (i) synthesis(!), (ii) thermophysical characterisation – using TGA/DSC/rheometry to measure stability, melting point, viscosity, density and chemical characterisation (NMR, IR, XRF etc), and then (iii) test materials for applications which will include cyclic voltametry and conductivity (EIS) for electrochemical uses and gas capture/solubility screening (with Dr Moura) to see whether there are, particularly, any uses in CO2 capture.

Progress to date

Literature review related to the sodium borates and sugar alcohol ethers (as sustainable solvents for generation of solvate IL electrolytes) has been undertaken. Synthesis of a systematic series of alkanolamines for the preparation of borates. Previous work was studied in detail to examine the possibility of alteration in the preparation of material to get better results.

Conclusions and future work

The future of borates ILs is in the innovation and collaboration in all the relevant discipline where cost effectiveness and sustainability are the key factors. New borates with enhanced properties with scalable manufacturing, low toxicity and cost effectiveness are highly required. The field is growing with promising borate ILs as versatile and ecofriendly alternative to conventional solvents and materials.

QUILL Quarterly Report

August - October 2024

Name:	Jamie Warren		
Supervisor(s):	Prof Gosia Swadzba-Kwasny and Prof Peter Nockemann		
Position:	PhD student (1st year)		
Start date:	1/10/24	**Anticipated end date:**	1/9/28
Funding body:	EPSRC/Ionic Technologies		

Circular Economy of Critical Elements: Waste Valorisation in Magnet Recycling Process

Background

The aim of this PhD project is to add value to a scalable and commercially viable magnet recycling process in partnership with QUILL and Ionic Technologies. NdFeB magnets sourced from end-of-life (EOL) products such as wind turbine generators and electric vehicle (EV) batteries provide a bountiful untapped supply of rare earth elements (REEs) to be recycled, repurposed and reused in further applications. The current mining of REE ores and their subsequent extraction poses geopolitical and environmental issues relating to their supply and use globally. In order to mitigate these issues, the direct recycling of REEs from EOL products has been proposed as part of the circular economy of these critical metals. Solvent extraction (SX) is a popular method used for the separation of REEs industrially, however, it poses numerous challenges including the generation of highly acidic wastewater, intensive reagent consumption and efficient separation of the elements requiring a very large number of extraction steps. Another key challenge in the separation of REEs using SX is the formation of interfacial phenomena such as gels and emulsions, which ultimately reduces the efficiency of each extractant step. Thus, the ability to improve the extraction and separation of REEs is a promising prospect for positively contributing to the transition towards Net Zero through developing a closed recycling loop for the recycling of the metals used in magnet applications.

Objective of this work

The ultimate goal of this project is to optimise the separation of adjacent heavy REEs through investigating the efficiency and selectivity of various solvent extractant systems that can potentially be used in an industrial setting. This will involve modulating the interfacial phenomena of the extraction phases and enhancing the properties of extractant ligands through synergistic effects, use of ionic liquid or deep-eutectic solvent additives or by synthesising new extractants. It is also hoped that any improvements to the process will prove to be more cost effective and less environmentally polluting.

Progress to date

Review of the current literature on industrial processes used for the separation of REEs. Performance of benchmark tests to establish a precedent with which to optimise the system parameters. Preparation for January Initial Review.

Conclusions and future work

Literature review for project is currently ongoing, as is benchmark testing of REE extraction at Ionic Technologies. It is hoped that an appropriate amount of data will have been collected to assess the current efficiency and selectivity of the solvent extraction process currently being employed within the company. Preparation for January Initial Review is also currently being carried out.

QUILL Quarterly Report

August - October 2024

Name:	Anna White		
Supervisor(s):	Dr Paul Kavanagh (primary) and Dr Leila Moura (secondary)		
Position:	PhD Student		
Start date:	1/10/24	**Anticipated end date:**	1/10/27
Funding body:	DfE		

Combining Electrocatalysts and Gas-Capturing Liquids for Electrochemical Conversion of CO_2 to Value-added Chemicals

Background

With the escalating urgency of the climate crisis, reducing atmospheric carbon dioxide (CO_2) levels has become a critical priority. One promising strategy for utilizing captured CO_2 involves its electrochemical reduction into value-added chemicals, such as methane and formic acid. However, the poor solubility of CO_2 in conventional electrolytes presents a significant challenge to this process.

Traditionally, amines have been the primary choice for CO_2 capture due to their high adsorption capacity, and their ability to serve as electrolytes for CO_2 reduction. Nevertheless, the inherent toxicity and corrosivity of amines have spurred researchers to explore alternative gas-absorbing liquids. Ionic liquids and deep eutectic solvents are emerging as attractive alternatives, thanks to their relatively low toxicity and dual functionality as both CO_2 absorbents and efficient electrolytes. These so-called "green" solvents show great promise for carbon capture and utilization technologies.

The electrochemical reduction of CO_2 faces two significant competing reactions: the hydrogen evolution reaction (HER) and the oxygen reduction reaction (ORR). Remarkably, ionic liquids and deep eutectic solvents have demonstrated the ability to suppress HER, thereby improving the efficiency of CO_2 reduction. This dual role of facilitating CO_2 capture and enhancing its electrochemical conversion makes these innovative solvents a focus of growing interest in the fight against climate change

Objective of this work

In this work, the electrocatalytic properties of a wide range of gas-capturing liquids will be investigated in terms of electrochemical efficiency, selectivity, and scalability. The project ultimately seeks to provide a method of carbon dioxide reduction using gas-capturing liquids and electrocatalysts.

Progress to date

The project has begun with intensive literature review, developing an in-depth understanding of the subject area. Specific attention has been dedicated to the ionic liquids and deep eutectic solvents that have been previously used for this purpose. From this, aqueous choline chloride solutions have been selected as the first electrolyte for further study. I am currently investigation the electrochemical windows and D/L capacitance of aqueous choline chloride solutions of varying concentration and comparing the choline chloride solutions to aqueous potassium chloride and tetramethylammonium chloride electrolytes.

Conclusions and future work

On first analysis, the aqueous choline chloride solutions present similar electrochemical properties to that of tetramethylammonium chloride solutions. Given the toxicity of tetramethylammonium chloride, the choline chloride solutions present an attractive alternative as electrolyte. Future work aims to compare the electrocatalytic properties of these choline chloride solutions to that of conventional potassium chloride solutions. Further analysis using electrochemical impedance spectroscopy, chronoamperometry and redox probe studies will be performed for all three electrolytes. As well as this, further characterisation of the aqueous choline chloride solutions is planned.