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QUILL
Quarterly Reports

November 2024 – January 2025

CONFIDENTIAL (up to January 2028)

Contents

QUILL Quarterly Report

November 2024 – January 2025

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 am work on synthesising new boron-containing ionic liquids such as tetrabutylammonium bis(glycolato)borate and etrabutylammonium bis(oxalato)borate. These studies are also continuing.

I presented QUILL conference through poster in 2nd of September. I was awarded the best poster award 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. I will present poster and oral presentations on QUILL meeting on 31st March.

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. The synthesis of $[P_{66614}]_2[Ln_2(Oct)_8]$ will be starting point of this research. 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

November 2024 – January 2025

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

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

Overview

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

Objective of this work

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

Work to date

As previously reported, full cell testing indicated an improvement in battery performance across each key metric (voltage efficiency, coulombic efficiency and energy efficiency) when using polyoxometalate-decorated graphite felt (POM-GF) as the negative electrode. Due to these encouraging results, it was decided to work towards a research paper. They key question was surrounding repeatability, therefore three batches of POM-GF were prepared and characterised electrochemically. These were tested in a three electrode set up sing Ag/AgCl in 3M KCl as reference electrode, Pt Mesh as counter electrode and 0.5 cm^2 graphite felt as the working electrode. The working and counter electrode were connected to tantalum clips ad the tests were conducted under N_2 atmosphere. As seen in fig 1. (a) POM-treatment consistently improves electrochemical activity and reversibility when compared to both pristine (P-GF) and heat-treated graphite felt (H-GF). No distinguishable peaks are observed for either P-GF or H-GF, where a clear reversible pattern is observed for each of the POM-GF. Upon comparison of the treated felts, it was observed that ΔE reached as low as 212.4 mV, indicating improved reversibility of the system. Fig 1. (b) and (c) highlight how peak current density increased linearly with increased scan rate, indicating that the reaction is diffusion limited.

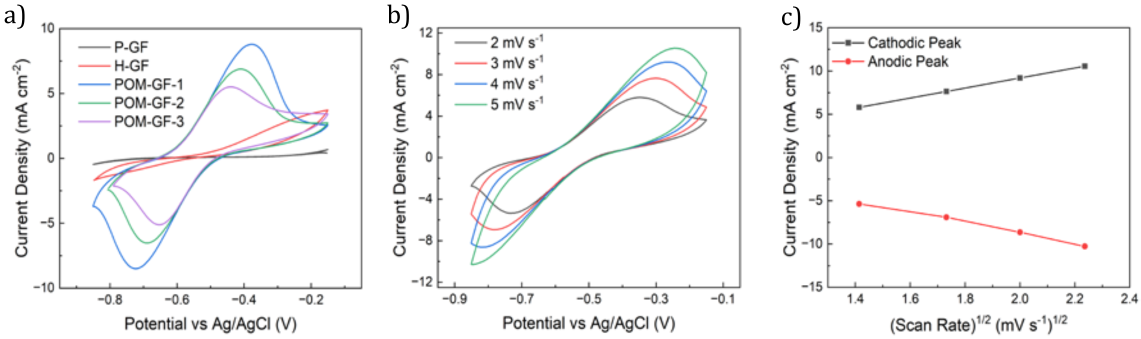

Figure 1 (a) - CV of GFs in 50mmol V(II) in 2M H_2SO_4 at 2 mV s^{-1} **(b)** CV of POM-GF at different scan rates **(c)** Plot of peak current versus square root of scan rate for POM-GF

	E_{pa}	E_{pc}	ΔE	I_{pa}	I_{pc}	I_{pa}/I_{pc}
POM-GF-1	-0.723	-0.377	0.346	-0.0021	0.0022	0.95
POM-GF-2	-0.68954	-0.40878	0.28076	-0.00163	0.00172	0.95
POM-GF-3	-0.65292	-0.44052	0.2124	-0.00128	0.00138	0.93

Table 1 - Key performance indicators of POM-GFs from CV scan

Conclusion and future work

To conclude, POM-GF consistently outperformed H-GF and P-GF in electrochemical performance when probed using CV. These tests will be repeated, utilising a pre-soaking method beforehand where the graphite felts to be treated will be subject to mechanical wetting prior to analysis. Cell tests will be conducted using POM-GF as electrode in negative half-cell three times to ensure repeatable battery performance improvements. POM-GF will also be re-tested in posolyte using the aforementioned pre-soaking method which may further improve performance.

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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

The urgent need for efficient carbon dioxide (CO_2) capture is central to achieving the goals of the Paris Climate Agreement and commitments made at COP29. Conventional industrial CO_2 capture methods, such as amine scrubbing, are widely used but suffer from major drawbacks, including high energy consumption, toxicity, and environmental concerns[1]. These limitations drive the demand for alternative technologies that are more sustainable and cost-effective.

This project explores the development of biobased porous liquids (PLs) as a novel approach to CO_2 capture. Porous liquids are an emerging class of materials that merge the high gas uptake capabilities of microporous solids with the fluidity of liquids[2]. Unlike traditional liquid sorbents, PLs maintain internal porosity within a liquid matrix, allowing for efficient gas capture and separation. Their adaptability and ability to operate under varied conditions make them highly attractive for industrial use.

Designed to be low-cost, non-toxic, and highly efficient, these PLs will integrate microporous solids derived from renewable biopolymers with non-volatile liquid carriers. Key materials include cellulose[3], chitosan[4], and cyclodextrins[5] - sustainable, biodegradable, and highly functionalisable polymers ideal for targeting specific gases. Their scalability and eco-friendly nature position them as strong candidates for commercial deployment.

By leveraging the unique properties of biobased components and the versatility of porous liquids, this research aims to develop next-generation CO_2 capture materials that align with global sustainability objectives. With the potential for widespread industrial application, biobased porous liquids offer a transformative solution for reducing carbon emissions and facilitating the transition to a low-carbon economy.

Objective of this work

The ultimate goal of the project is to develop sustainable, biobased porous liquids designed for efficient gas capture and separation, offering a cost-effective 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, I have successfully synthesised multiple samples of cyclodextrin-based metal-organic frameworks (CD-MOFs) and begun preliminary characterisation to assess their structure and gas uptake potential. For the cellulose nanofiber foams, I have ordered all necessary chemicals and am finalising the preparation steps for synthesis. Alongside these developments, I have completed training on powder X-ray diffraction (PXRD) and have also started familiarising myself with the gas rig setup, ensuring I can efficiently conduct adsorption and separation studies in the coming months.

As part of the CDT PhD program, I attended an introductory session in Birmingham, where I gained insights into key research themes and collaborative opportunities within the cohort. Additionally, I completed a Responsible Research and Innovation (RRI) course at the University of Nottingham, which provided a deeper understanding of the ethical and societal considerations surrounding scientific research. These experiences have enhanced my technical skills and broader research perspective, equipping me to progress towards optimising these bio-based materials for efficient gas capture and separation.

Conclusions and future work

The next phase of the project will focus on detailed characterisation and performance evaluation of the synthesised materials. This includes conducting thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), and Brunauer-Emmett-Teller (BET) surface area analysis to assess material stability, crystallinity, and porosity. CO_2 uptake measurements will be performed using headspace gas chromatography (HS-GC) to determine the gas capture efficiency of the CD-MOF samples.

In parallel, I will begin the synthesis of cellulose nanofiber foams, optimising processing conditions to ensure reproducibility and performance. Additionally, the synthesis of porous liquids will start using non-ionic liquids such as triglyceride oils, with stability and CO_2 uptake assessments to determine their potential for gas separation applications. These studies will help refine material selection and processing methods to develop efficient and scalable gas capture solutions.

As part of the CDT PhD programme, I will also be attending a Negative Emissions Technologies course at the University of Warwick in March, which will provide further insights into emerging CO_2 removal strategies. Additionally, I will participate in Life Cycle Analysis (LCA) training at Queen’s University Belfast, equipping me with the skills to assess the environmental impact of the materials and processes being developed. These courses will support a more comprehensive approach to my research, integrating sustainability considerations and real-world applicability.

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5. I. Roy, J.F. Stoddart, *Accounts of Chemical Research* 2021, 54, 1440–1453.

QUILL Quarterly Report

November 2024 – January 2025

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.

Furthermore, we noticed that many electrophotocatalysts have very low lifetimes, yet still are able to carry out reactions – because of this we wanted to probe the mechanism.

Objective of this work

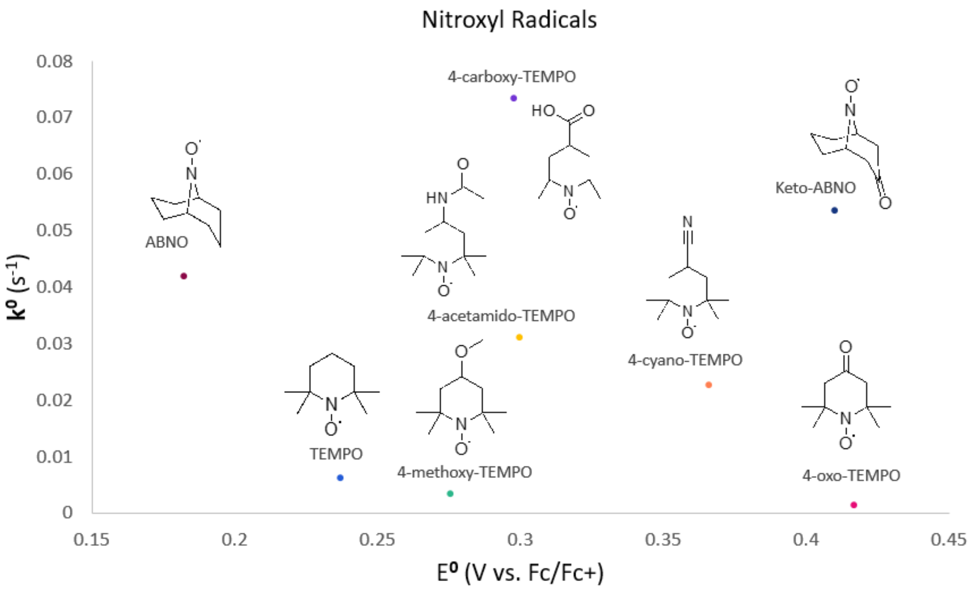
The plan is to study a series of homogeneous redox electrophotocatalysts, specifically reductive electrophotocatalysts. By activating these catalysts though applying a negative potential and exciting them using light, they will have a very high energy that ideally will be used to reduce more difficult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

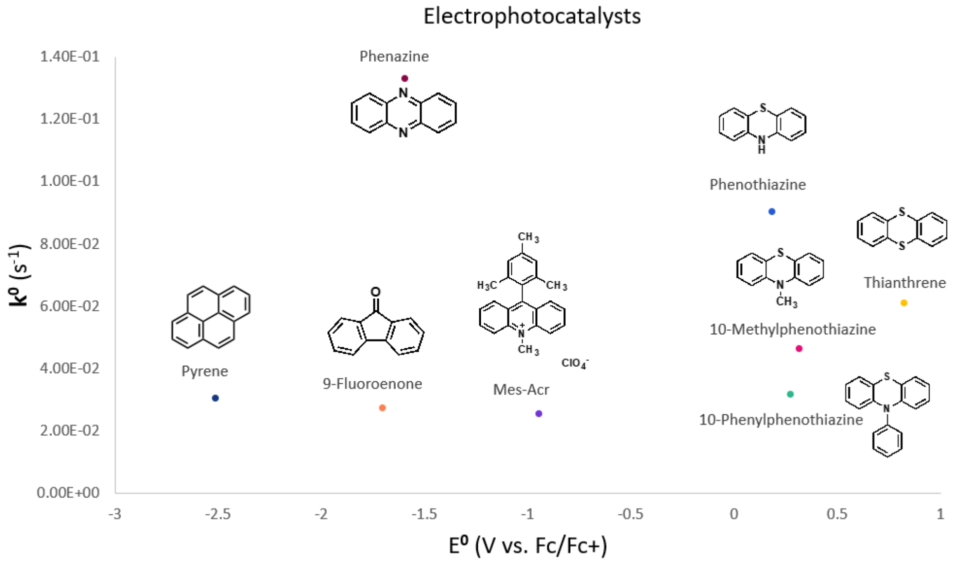
Progress to date

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.

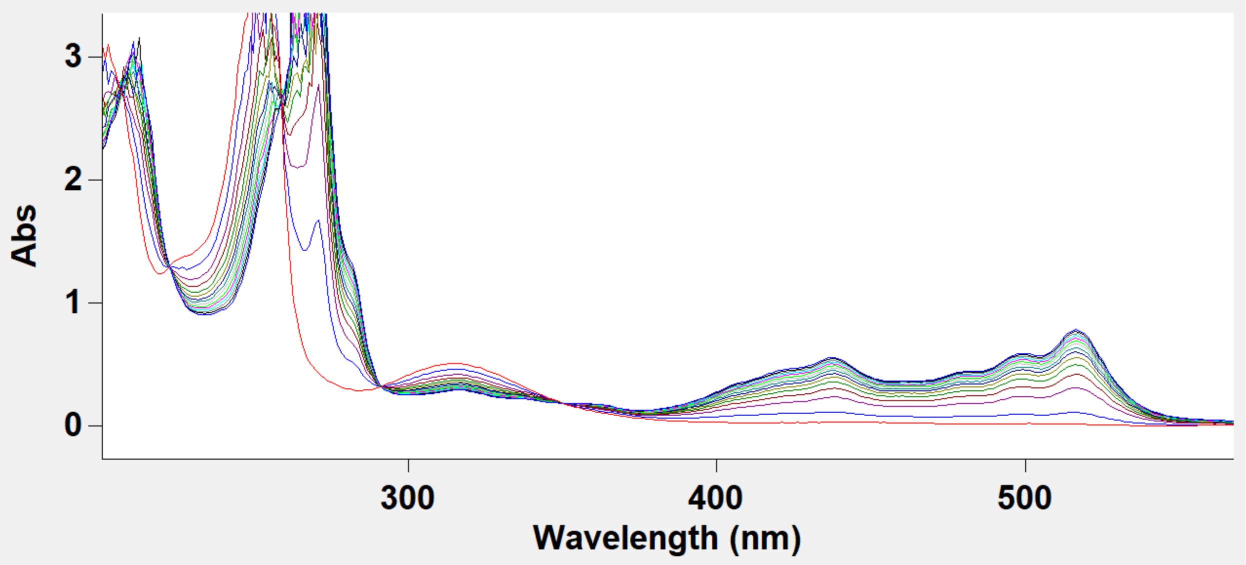
However, we have noticed that there seems to be a lot of disparity between values reported in papers on these parameters, and that they are difficult to reproduce. We believe they are not measured as accurately as they could be, and that alternative methods should be used. Previously, only cyclic voltammetry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

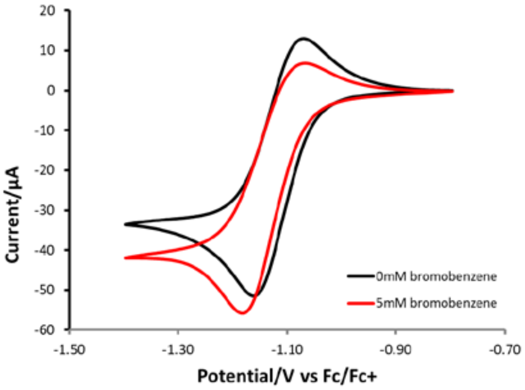


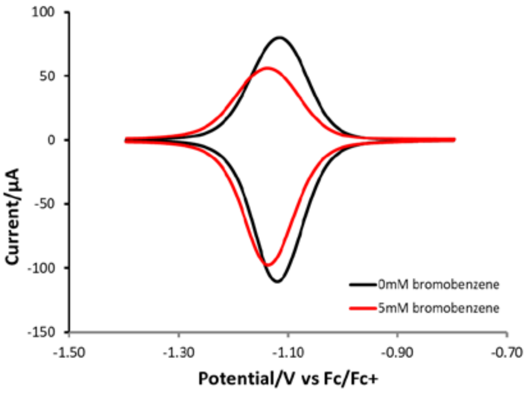


Furthermore, preliminary studies have begun on the photochemistry part of the reaction. UV/Vis spectroelectrochemistry has been used, to monitor the change in absorption wavelength of a selection of common electrophotocatalysts as they are being oxidised/reduced. Using these results, we can find the 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:

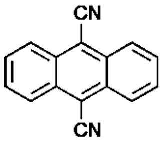


We then noticed how the reported lifetimes of many electrophotocatalysts are very small – not long enough for reactions to be carried out, yet the reactions still proceed. We decided to probe this mechanism using CV and square wave voltammetry (SWV).

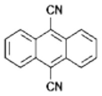




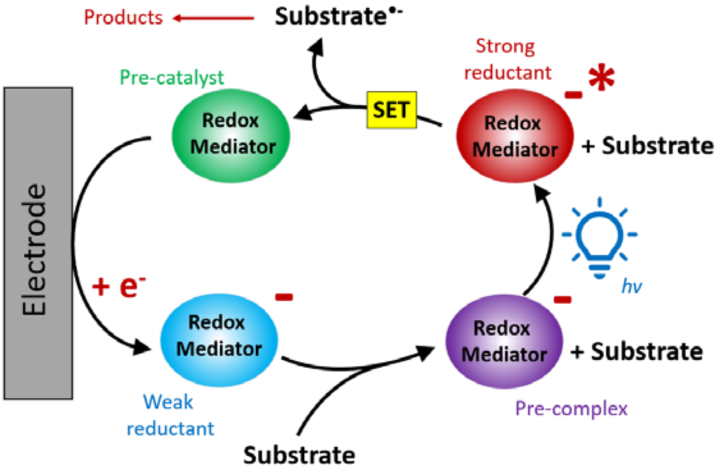
Catalyst:



Substrate:



We found that there is a shift in the potential in the CVs before and after the substrate was added, carried out under no light. This indicates that there is precomplexation between the catalyst and the substrate before the catalyst is then irradiated. This indicates a change in the understood mechanism of electrochemistry, which allows us to propose a new mechanism:



Conclusions and future work

I want to finish writing the paper for the CV and RDV study on electrocatalysts - 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. The study on probing the mechanism will continue, ideally using another method such as NMR to confirm the results. Ideally a paper will come from this study as well.

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 to see if it is successful.

QUILL Quarterly Report

November 2024 – January 2025

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 available storage systems, 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 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^2g^{-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 like 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 how optimising the compression of the modified graphite felt electrodes within an iron and vanadium redox flow battery improves power density.

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 liquids and the optimisation of electrode compression.

Progress to date

In the last quarterly report, it was found through CHN elemental analysis that the carbon created from choline glycinate ([Ch][Gly]) after pyrolysis (800 °C, 2 hours, nitrogen atmosphere) had the elemental composition presented in Table 1.

	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 created from [Ch][Gly]

From these results, it was encouraging to observe a 5 at.% of nitrogen within the carbon, as 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. However, the fact that 65 at.% was unaccounted for suggests that a large proportion of it is probably composed of potassium chloride (KCl), which is a by-product of the synthesis of [Ch][Gly].

To explore this further, the carbon powder was observed under a scanning electron microscope (SEM) and the images that were obtained are presented in Figure 6. Initially, as seen in Figure 6a, it is observed that a porous carbon powder has been created. However, as the magnification is increased (Figure 6 b - d) and the contents of the surface of the carbon are revealed, it becomes clear that it is entirely coated in the characteristic cubic crystals of KCl that are approximately 8 - 20 µm in size. With this new knowledge, the SEM images presented in the last quarterly report were reviewed again and it was clear that potassium chloride crystals were also being doped onto the surface of the modified graphite felts. For example, Figure 1 is an annotated SEM image which highlights the KCl present on the surface of a graphite felt fibre after modification.

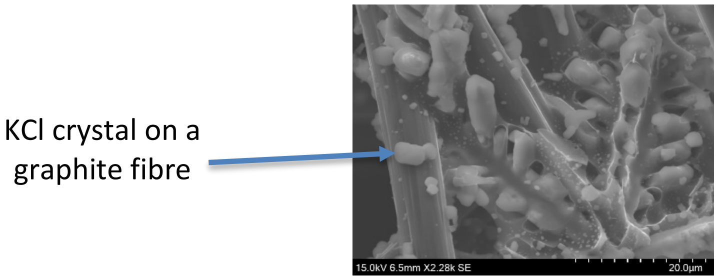


Figure 1 - KCl crystals present on the surface of [Ch][Gly] modified GF

In light of this, post-treatments were applied to the modified electrodes to observe if improvements in performance could be attained if KCl was removed from the surface of the fibres. Specifically, three different post-treatment strategies were employed and these were a "flush" of distilled water in a Buchner funnel, allowing the modified felt to soak in distilled water for 20 minutes and no post-treatment. These post-treatments were implemented on GF:[Ch][Gly] = 1:1.5 as it was determined to be the best performing felt from the mass ratio study presented in the previous quarterly report. The cyclic voltammograms for the post-treated electrodes are presented in Figure 2 and there is a negligible difference between the performance of the electrodes. Therefore, either KCl is having a small impact on performance or the post treatments that were used were unsuccessful in removing the potassium chloride. The latter is most likely the case because of how incorporated KCl is within the structure of the carbon material created.

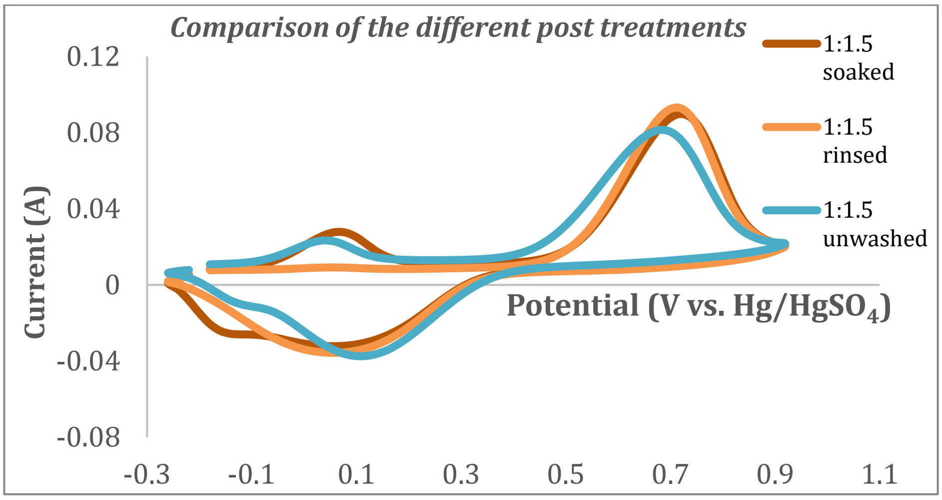


Figure 2 - Cyclic voltammograms of the post treated GF:[Ch][Gly] = 1:1.5 felts

An unforeseen result of this study was that there was a significant reduction in electrochemical activity observed across only five cyclic voltammetry cycles and this can be observed in Figure 3. While there has been no formal investigation into why this is occurring it is predicted that the KCl crystals present in the carbon material are dissolving in the vanadium electrolyte and removing part of the carbon decorated onto the surface of the graphite felt, which is causing a steady reduction in electrochemical performance.

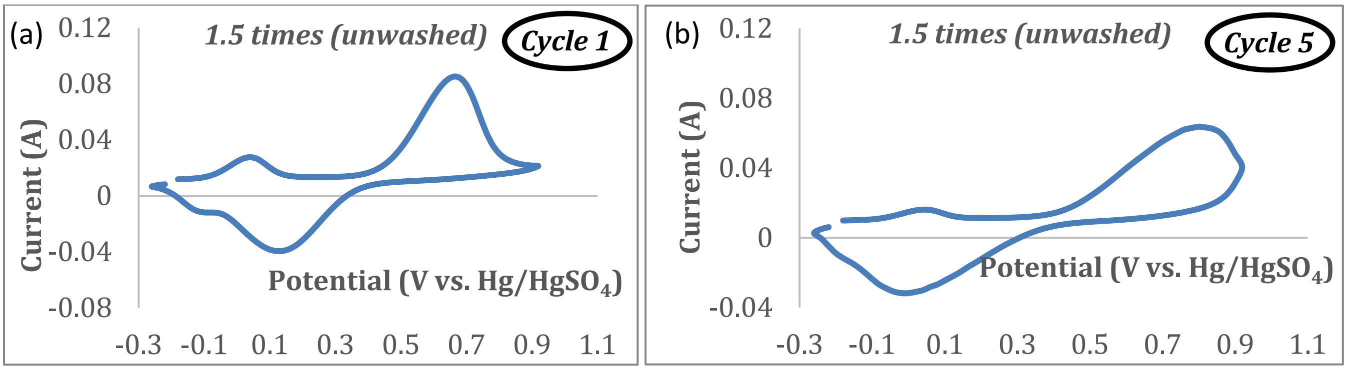
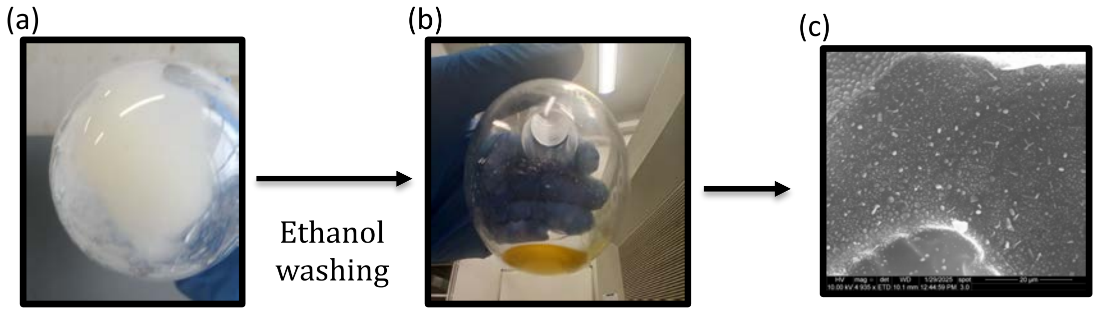


Figure 3 - Cyclic voltammogram of (a) GF:[Ch][Gly] =1:1.5 (unwashed) after one cycle and (b) GF:[Ch][Gly] = 1:1.5 (unwashed) after five cycles

Due to the combination of the failure of the post treatments to significantly improve electrode performance and the observed cycling instability, it was determined that it would be best to remove the KCl from the [Ch][Gly] before it was converted into a carbon powder by repeatedly "washing" the ionic liquid with ethanol to precipitate out the KCl crystals present. As seen in Figure 4, significant visual improvements to the purity of the ionic liquid were obtained but whenever this ionic liquid was converted into a carbon material, SEM images revealed that potassium chloride crystals were still present but were smaller than the 8 - 20 μm size observed previously.



Unwashed [Ch][Gly]

Washed [Ch][Gly]

[Ch][Gly] powder with KCl crystals

Figure 4 - Scheme with an image of (a) unwashed [Ch][Gly], (b) ethanol washed [Ch][Gly] and (c) a SEM image of the carbon powder created from [Ch][Gly] with KCl crystals on its surface

While it would be possible to test the performance of this purified ionic liquid, it was decided that [Ch][Gly] will be synthesised using an entirely different methodology to avoid the formation of KCl. Specifically, this reaction pathway involves reacting glycine with choline hydroxide through the reaction scheme that is presented in Figure 5. The improvements in performance that should be yielded from the shift to this reaction pathway will be shown within the next quarterly report.

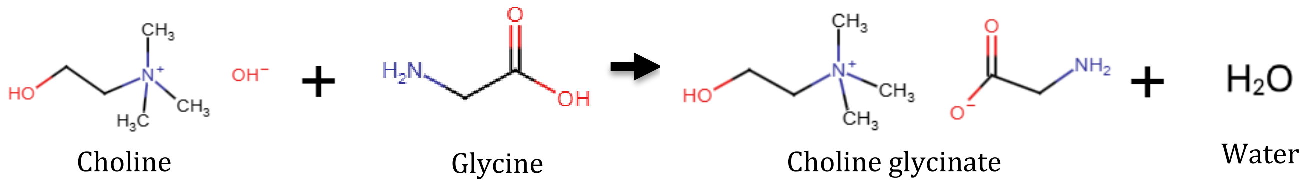


Figure 5 - Reaction scheme for the synthesis of choline glycinate using choline hydroxide and glycine

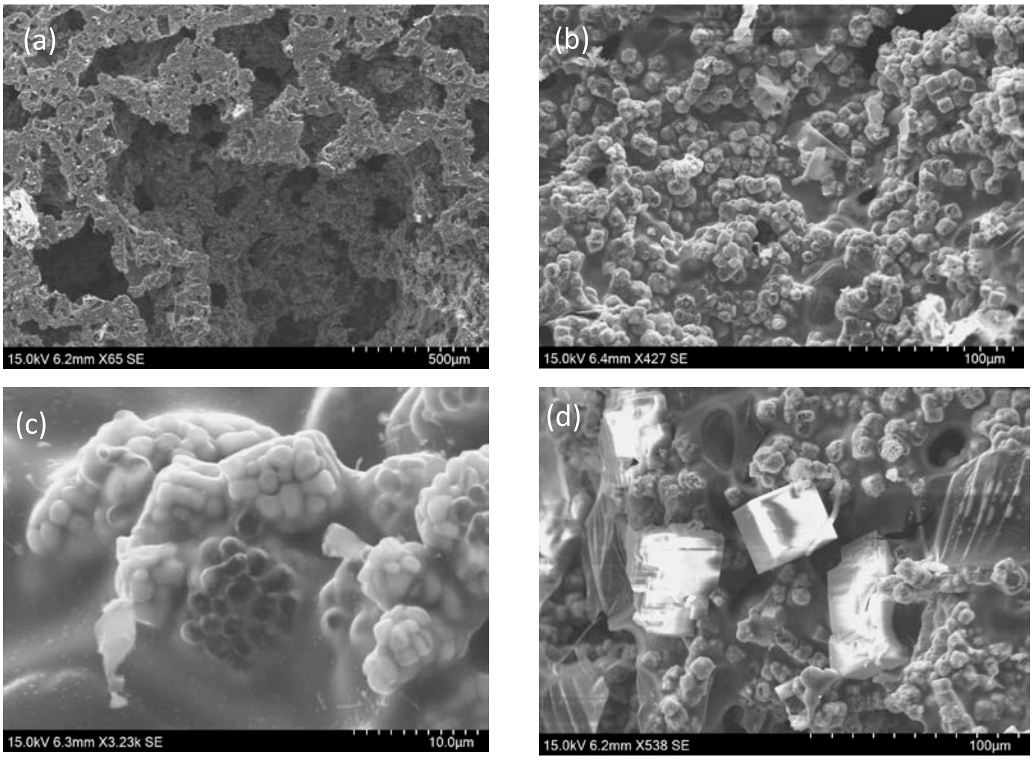


Figure 6 - SEM images of carbon powder from [Ch][Gly]. Specifically, (a) a low magnification image (b) a moderate magnification image, (c) a high magnification image, (d) a second high magnification image

Conclusions and future work

It was found that the prediction made in the last quarter that a large proportion of the carbon created from [Ch][Gly] is composed of KCl was correct and this was confirmed through SEM imaging. The presence of this water soluble crystal in the carbon material was attributed to the poor cycling stability of the [Ch][Gly] modified electrodes on the basis that it may be removing the decorated carbon material as it dissolves in the vanadium electrolyte. KCl was unsuccessfully removed through a variety of electrode post treatments and by attempting to "wash" the ionic liquid before pyrolysis using ethanol. Therefore, going forward [Ch][Gly] will be synthesised using choline hydroxide instead of choline chloride which means that the formation of KCl will be entirely avoided.

Future work will be focussed on finding the best GF:[Ch][Gly] mass ratio for the choline glycinate synthesised using choline hydroxide. Additionally, it is hoped that improvements to electrochemical performance and cycling stability will be observed for this new carbon material. After this, a pyrolysis temperature study between 800 - 1200°C will be conducted to find the best temperature for nitrogen doped carbon creation. Finally, the best performing modified felt after these studies will be put into a single cell battery to observe the improvements in capacity, coulombic efficiency, voltage efficiency and energy efficiency that can be obtained compared with untreated GF.

QUILL Quarterly Report

November 2024 – January 2025

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 ionic liquids have been made 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 (1-

MN) 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] and C_4CNPyr[NTf_2] ILs and also the mixtures of these ILs with 1-methylnaphthalene. Also, I have repeated each of the EIS experiments to confirm specific trends that were observed upon the addition of the dilutant 1-MN (forms a CTM complex in situ). I also performed multiple viscosity measurements on the individual ILs and 1:1 IL/1-MN mixtures. This was done to understand whether increases/decreases in conductivity were due to improved diffusivity within the salts, depending on what was seen in both sets of EIS/ viscosity data. As upon the addition of a traditional dilutant e.g. organic solvent etc. there is a decrease in viscosity and therefore a rise in conductivity. However, upon the addition of 1-MN to the ILs there is not an increase in conductivity, and we believe that this is due to the strong pi-pi stacking and ion pairing between these ILs and the charge donor molecule 1MN. From the viscosity measurements that were carried out there was a decrease in viscosity upon addition of the 1-MN. This was expected as upon adding a dilutant or simply a liquid to another viscous liquid it will obviously decrease the viscosity. 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. We devised a final thesis chapter plan too and decided I will have 7 chapters in total, to include 5 research chapters. I have also begun writing my thesis and that is going great and is very enjoyable. I plan to hopefully have it submitted by end of May/June, as I am writing and finishing lab work simultaneously.

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 will carry out an EIS experiment with one of the cyanopyridinium ILs + an organic solvent to show how typical dilutants do in fact increase conductivity, to act as a nice comparison to the data that we have already gathered. I also hope to finish my thesis ASAP and hopefully have publications from three of the primary research chapters.

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QUILL Quarterly Report

November 2024 – January 2025

Name:	Ayantika Kundu		
Supervisor(s):	Dr Marijana Blesic and Dr Matthew Wylie		
Position:	PhD student		
Start date:	November 2024	**Anticipated end date:**	September 2027
Funding body:	DfE International studentship		

Development of Innovative Multifunctional Zwitterionic Materials for Application in Healthcare and Energy Sector

Background

Antimicrobial resistance is one of the most pressing global challenges of our time, posing significant threats to public health and necessitating innovative and multifaceted solutions. Traditional approaches, such as the development of new medications, while essential, are no longer sufficient on their own. A complementary strategy involves the implementation of preventive measures, particularly through the application of advanced surface coatings designed to combat biofilm formation. Biofilms, which can harbour resistant bacteria, often develop on the surfaces of medical devices, leading to persistent infections and increased reliance on antimicrobial therapies. By engineering multifunctional self-cleaning, protein-resistant, antifouling, and antibacterial coatings, this project aims to reduce the frequency of such infections, thereby lessening the dependence on antimicrobial drugs and curtailing the rise of resistance.

At the core of this approach is the use of zwitterionic materials, which possess both positive and negative charges within the same molecular structure. This unique characteristic endows the materials with exceptional properties, including the ability to repel bacteria and prevent the adhesion of contaminants, ultimately contributing to a self-cleaning surface. The research will focus on tailoring these zwitterionic coatings to enhance their performance in medical settings, ensuring that they are effective against a wide range of pathogenic organisms while being compatible with various device materials.

In parallel, the project seeks to address significant challenges in the energy sector, particularly those associated with zinc-ion batteries. Zinc-ion batteries are recognized for their high theoretical specific capacity, low cost, safety, and environmental benefits, making them promising candidates for large-scale energy storage applications. However, their commercialization is hindered by issues such as detrimental electrochemical reactions occurring at the cathode and anode interfaces. These reactions lead to reduced cycling life and overall battery instability, limiting their practical usage.

To overcome these obstacles, the project will leverage the multifunctional properties of zwitterionic materials by integrating them as electrolyte additives or interfacial adsorbents in zinc-ion batteries. The incorporation of these materials is anticipated to suppress undesired electrochemical reactions and promote the dissociation of salt within the electrolyte.

Additionally, their unique molecular architecture is expected to facilitate the formation of channels that enable rapid ion transport, thereby enhancing the battery's performance and longevity.

By simultaneously advancing the fields of antimicrobial coatings and energy storage, this project embodies a holistic approach to addressing critical challenges in healthcare and sustainability.

Objective of this work

The goal of this project is to create novel multipurpose zwitterionic materials for two important uses: improving the performance of zinc-ion batteries and creating antimicrobial coatings for medical equipment. Designing self-cleaning, protein-resistant, antifouling, and antibacterial coatings for medical equipment is intended to reduce the need for antimicrobial-drug therapy by preventing the formation of biofilms. By employing zwitterionic materials as interfacial adsorbents or electrolyte additives, the energy sector hopes to improve the electrochemical performance of zinc-ion batteries. This will increase ion transport, stabilise electrode interfaces, and prolong battery life. In the end, our study aims to use the special qualities of zwitterionic materials to address global issues in energy storage and healthcare.

Progress to date

1) ADS-M812- The study aimed to investigate the aggregation behaviour of aluminium distearate (ADS) in M812 using ^{1}H and ^{27}Al NMR spectroscopy. Initial solubility tests revealed that ADS was insoluble in all tested polar deuterated solvents, and its proton peaks overlapped with those of M812, complicating spectral analysis. Despite attempts to detect ADS aggregation at various concentrations, overlapping signals and low solubility hindered the identification of distinct proton peaks. Furthermore, ^{27}Al NMR spectra exhibited broad aluminium peaks, obscuring potential shifts due to aggregation. Similar results were observed when ADS was tested in n-octane, indicating that NMR spectroscopy was ineffective in studying ADS aggregation in M812.
2) Designing zwitterionic surfaces with antimicrobial, protein resistant properties- In the QCM experiments, sensors were functionalised with C12 Thiol, single zwitterions, and double zwitterions to evaluate their protein-resistant properties using lysozyme protein in a pH 7.4 buffer. Measurements of frequency and dissipation were recorded at a constant temperature of 23°C. As anticipated, the hydrophobic C12 Thiol exhibited the highest protein absorption, while SZW and DZW, being progressively more hydrophilic, showed reduced absorption. However, the differences in protein absorption among the sensors were not conclusive because of massive hydration found for double zwitterions.
3) Design of an organic compound to be used effectively in zinc-ion batteries- In this experiment, two parallel synthetic pathways are being explored to design an organic compound for zinc-ion battery applications. The first pathway utilizes fluoro alcohol, which is subsequently reacted with an amine to obtain the desired product. The second pathway follows an identical procedure, substituting fluoro alcohol with 1-dodecanol. The initial reaction step has been successfully completed for both pathways, and the second step is currently in progress.

Conclusions and future work

The studies conducted so far have provided critical insights into material behaviours across different applications. The ADS-M812 aggregation study concluded that NMR spectroscopy was ineffective due to overlapping signals and solubility limitations. In the QCM experiments, zwitterionic surfaces demonstrated some level of protein resistance, though not as significantly as expected, indicating a need for further sensor optimization. Moving forward, the next steps include re-evaluating protein interactions with a different protein than lysozyme. It will be performed on the same sensors having functionalised with C12 Thiol, SZW, DZW. The zinc-ion battery project has successfully completed the first synthetic step, with the second step in progress. The aim is the complete the synthesis through both the route and move on to its application in zinc-ion battery.

QUILL Quarterly Report

November 2024 – January 2025

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 has been developed to directly consider several EV specific concerns and attributes. These include looking at four possible EV scenarios including Crash, parked, driving and charging scenario. Furthermore, a staggered module level array layout as well as EV style liquid cooling were also both considered. This has allowed a number of different materials with a range of cell to cell spacing to be considered. It was clear from these simulations that the crash and parked scenarios represent some of the most likely to cause widespread failure.

A more detailed criteria for the point of failure of a Li-ion cell has also been considered across a wide range of different array designs. This criteria has the potential to allow a more complete comparison between different array designs to be completed, allowing a better comparison of the method employed.

Additionally, fundamental heat transfer aspects of the model have also been validated against the physical rig. This includes looking at each of the fundamental heat transfer mechanisms helping to ensure that the input values that ae used are representative of reality. Furthermore by conducting this validation several practical considerations were brought to light including the consideration of contact resistance.

Conclusions and future work

Validation against the physical rig has been conducted and the simulations develop to near the point of completion. At this stage the range of materials that are applicable to propagation prevention must be assessed for weight and volume impact across the most dangerous EV scenarios. This will allow the most promising materials to be found and assessed.

QUILL Quarterly Report

August - October 2024

Name:	Daniel McCormack		
Supervisor(s):	Prof Peter Nockemann, Dr Oana Istrate and Dr Paul Kavanagh		
Position:	PhD Student		
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 longer lasting than 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 continued my lab work by making up six 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. I have used iron(iii) sulfate as a salt for forming the Fe(BIS-TRIS) salt because it allows for supporting electrolyte concentration in solution to be more finely controlled by crashing out barium sulfate.

I used the vapour diffusion technique to attempt to crystallize out Fe(BIS-TRIS) complex. These crystals require further study to determine their structure using singe crystal XRD.
I have taken successful CV scans of the six solutions of Fe(BIS-TRIS) I prepared. I have shown that the solutions undergo reduction and oxidation reversibly between potentials of -1.8 and -0.2 vs Hg/Hg_2SO_4 reference electrode.

Conclusions and future work

My CV scans have shown that increasing base concentration while maintaining a constant concentration of Fe ions and BIS-TRIS ligand in solution causes the Fe(BIS-TRIS) solution to undergo redox reactions more reversibly and with faster reaction kinetics while maintaining a high stability for 25 CV scans. This improvement in reactivity could be caused by improved formation of the Fe(BIS-TRIS) complex, or simply by the higher pH of the solution favouring the electron transfer reaction at the electrode surface.

To gain further clarity on the nature of these results by taking an EIS scan of each of the six solutions immediately before taking CV scans of the six solutions. Take EIS scans starting at a frequency of $1x10^5$ Hz and finishing at 0.1 Hz with amplitude 0.01 V_{RMS} and use the RelaxIS software to calculate the Solution resistance of each solution so that this can be accounted for in each CV scan using the I r drop correction function in the Nova software. This should give the most accurate CVs so that redox potential and peak separation can be accurately calculated.

Attempt CV scans with solutions having a 1:100 Fe(BIS-TRIS) to supporting electrolyte molar ratio, so as to ensure an accurate investigation of the Fe(BIS-TRIS) complex rather than solely investigating the overall solution properties.

Using what I have learned from of EIS and CV techniques I shall characterise the redox properties and stability of the MnO_4^- /MnO_4^{2-} redox couple.

Use the CCDC database to do a structural search to see if the crystal structures of Fe(BIS-TRIS), Fe(NTMPA), Fe(EDTMP) and Fe(DTPMP) have already been characterized before making up these complexes in solution and testing their redox properties by CV.

QUILL Quarterly Report

November 2024 – January 2025

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.

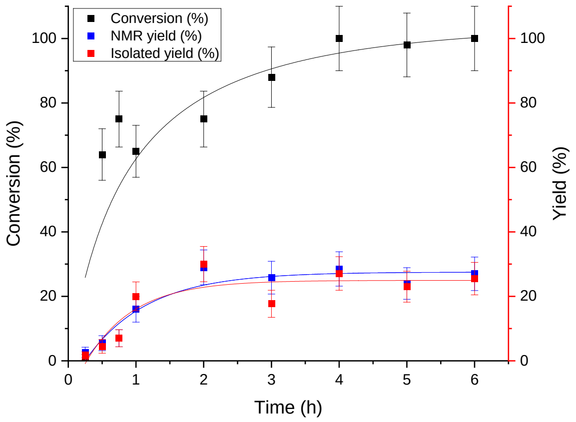
Objective of this work

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

November 2024 – January 2025

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

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

Background

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

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

Objective of this work

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

Progress to date

In November and December, I continued to prepare samples for a ISIS beamtime which is studying FLP on a solid support. I have tried to synthesis ^{11}B-BCF which was ultimately unsuccessful and we used normal BCF instead, we also tried to deuterated tri-tert-butylphosphine which was also unsuccessful so we decided to switch base to 2,6-lutidine. I also made some deuterated ionic liquids, along with the help of Aloisia 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.

Then it was a Grignard reaction from that trimethylborate and EtMgBr which had been changed to (C6F5)MgBr.

The phosphine was also using a Grignard reaction.

I then attended this beamtime in December with Beth and Malka and we ran the samples.

In January I had a beamtime at Diamond Light Source which was studying a range of boron lewis acids with 2,6-lutidine in an ionic liquid, so the majority of this month was spent preparing samples for this and then attending this beamtime.

Additionally in this month I started to write my paper of the previous x-ray data collected a year previously. I had a meeting with Diamond staff to discuss how we write this paper and what the focus of it will be.

Throughout this month I also had a meeting with Dr. Dingwall and other PhD students who are using python in their work as a way to advance these skills, I found this meeting very useful and we are going to be continuing these in the future.

Additionally in January, I demonstrated CHM1102 lab classes and am a tutor for a tutorial group.

Conclusions and future work

During this quarter, I carried out a lot of synthesis for a number of different beamtimes including the ISIS beamtime in December and Diamond beamtime in Janraury and I have started writing a research paper

Going forward, I will be continuing synthesis of these sampled for ISIS beamtime in May, and ESRF beamtime in June, however my main focus will be trying to complete the research paper, and also analyse the data from the two recent beamtimes.

QUILL Quarterly Report

November 2024 – January 2025

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 (REEs) is continually growing, as they are essential for the transition to more sustainable and green energy resources. These elements possess unique physicochemical properties, making them indispensable in applications such as wind turbines and electric vehicles. However, mining of the rare earths from their ores is not sustainable due to the large amounts of energy required and the limited availability of primary sources. China is the main supplier of REEs, but as demand increases, other countries cannot solely rely on exports to meet their needs. Therefore, producing REs from secondary sources (such as end-of-life NdFeB magnets) presents a more sustainable approach.

Solvent extraction emerges as the main process for recycling end-of-life magnets due to its advantages such as continuous operation, high capacity and efficient separation performance. This process has proven effective in separating the ‘light’ REEs from the ‘heavy’ REEs using traditional extractants. However, large amounts of acids or bases are typically required, along with the use of hazardous and volatile solvents. As a result, ionic liquids are considered to be a ‘green’ alternative due to their low volatility and flammability.

Separating adjacent REEs (e.g. neodymium and praseodymium) is challenging due to their similar ionic radius, ionic charge and coordination environment. The highest separation factor for Nd/Pr reported so far in the literature is 3.5 (Sun et al., 2019), although an increase in selectivity is often accompanied by a decrease in extractability. This is where the use of additives (ionic liquid or non-ionic liquid) enhances the properties of conventional extractants, resulting in a more efficient separation process.

Objective of this work

This project is in partnership with Ionic Technologies, and the aim is to develop and optimise an environmentally sustainable ionic liquid-based extraction system for the separation of neodymium and praseodymium from end-of-life NdFeB magnets. This will be achieved by establishing baseline performance metrics for several organophosphorus extractants, followed by investigating and characterising novel ionic liquids and their impact on extraction efficiency and selectivity for Nd/Pr separation. This will lead to developing and evaluating synergistic extraction systems combining conventional extractants with ionic liquid additives to enhance extractability and selectivity. Finally, the process parameters for a continuous counter-current extraction system will be mathematically modelled and optimised using COMSOL simulations, along with conducting a comprehensive techno-economic analysis to assess the industrial viability of the process.

Progress to date

To date, baseline performance metrics have been established for two conventional organophosphorus extractants (P507 and D2EHPA) in REE separation through systematic characterisation and optimisation studies. It was found that D2EHPA generally has a higher extraction efficiency, but lower selectivity compared to P507. The effect of saponification and organic to aqueous phase ratio (O:A) was also investigated for these two extractants, confirming that higher saponification rates (30%) and higher O:A ratio (5:1) resulted in more efficient extraction.

The ionic liquids [A336][P507] and [A336][D2EHPA] have been synthesised and characterised using XRF and NMR and are being used in extraction experiments in varying ratios to determine the impact on extraction efficiency and selectivity. The addition of Aliquat 336 (up to 30%) to P507 resulted in an increase in extractability but a slight decrease in selectivity compared to the extractant on its own. The effect of saponification of D2EHPA in [A336][D2EHPA] is also being investigated to determine the interactions within the ionic liquid and the effect on the extraction mechanism.

Conclusions and future work

The mechanism of extraction and the species formed during the extraction process with [A336][P507] will be investigated further using NMR, mass spectrometry and SAXS, to explain the increase in extractability. Future work will also involve investigating and characterising more conventional extractants with ionic liquid additives and investigating the extraction mechanism which will enable additional novel ionic liquids to be developed and characterised with different combinations of cation/anion to enhance the selectivity. There will be a specific focus on bifunctional ionic liquids, and ionic liquids using the hydrophobic, non-fluorinated anion, Aerosol-OT. Several extractant systems will then be used for batch counter-current work to determine the number of stages required for complete extraction and separation.

QUILL Quarterly Report

November 2024 – January 2025

Name:	Beth Murray		
Supervisor(s):	Prof Małgorzata Swadźba-Kwaśny and Prof John Holbrey		
Position:	PhD Student		
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 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]

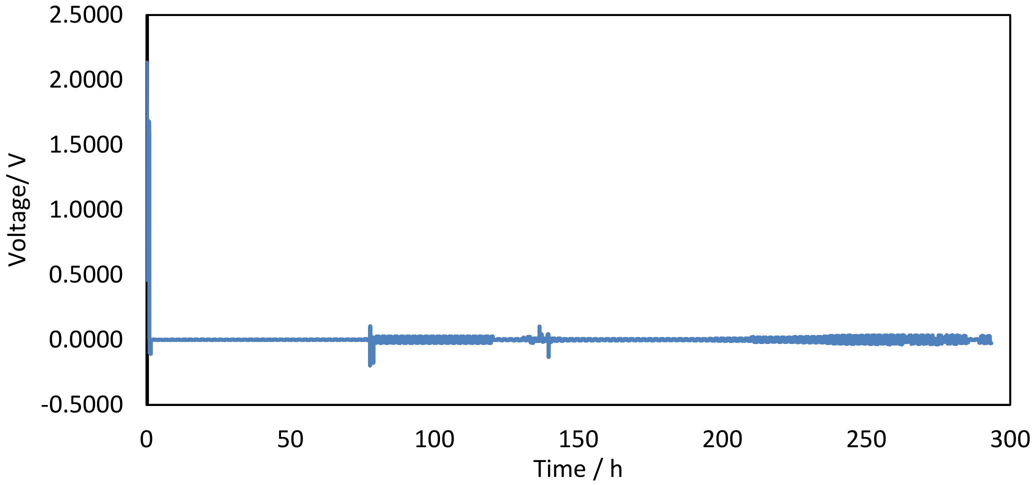


Figure 1 - Galvanostatic cycling of Al/Al symmetrical cell with urea-$AlCl_3$ electrolyte.

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).

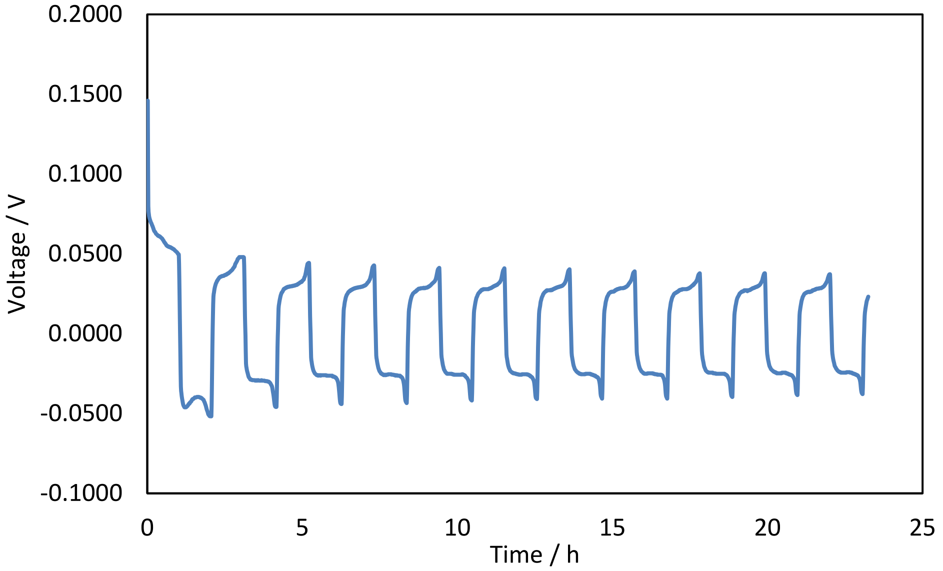


Figure 2 - Galvanostatic cycling of Al/Al symmetrical cell with urea-$AlCl_3$ electrolyte, after the Al electrodes were polished with acid.

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).

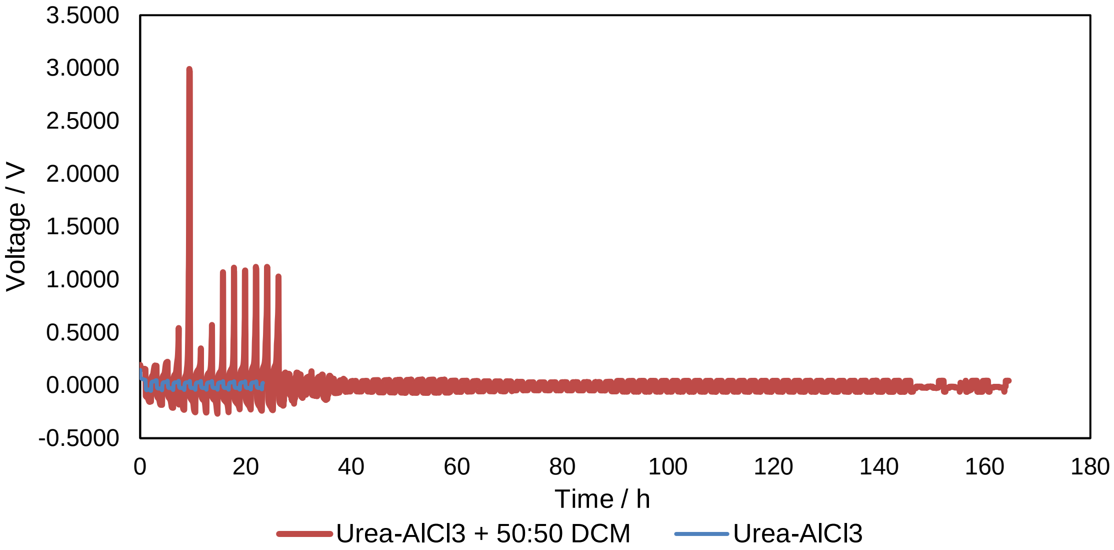


Figure 3 - Comparison of symmetrical Al/Al cycling with urea-$AlCl_3$ electrolyte and urea-$AlCl_3$ electrolyte with the addition of equimolar amounts of DCM

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.

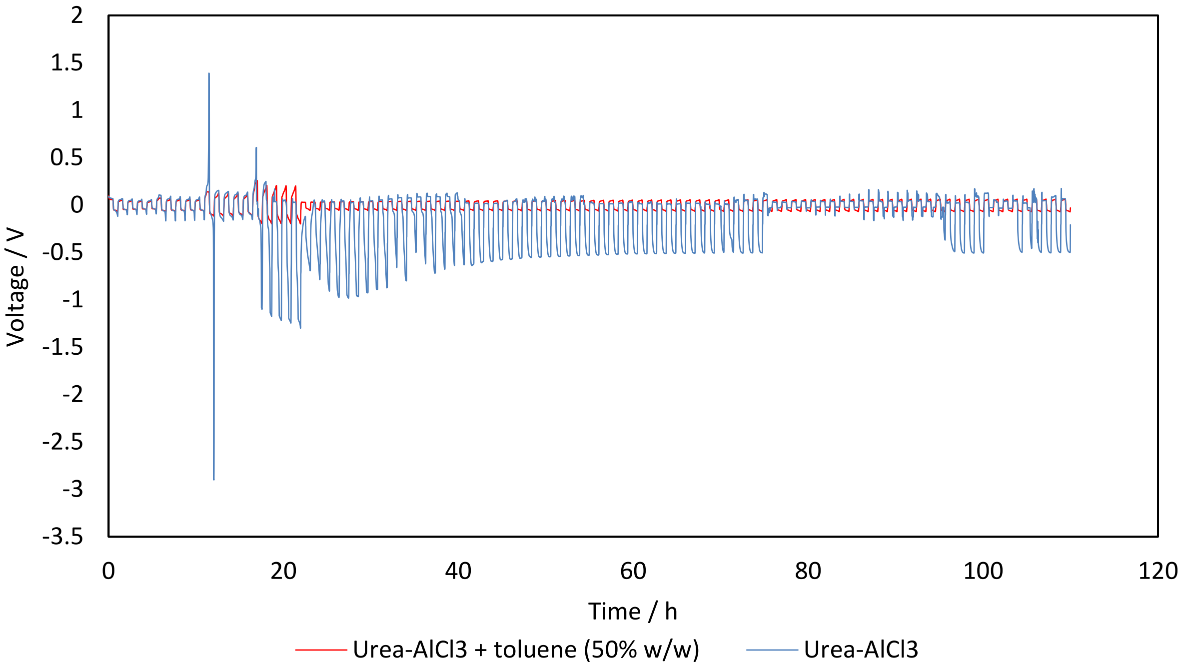


Figure 4 - Comparison of symmetrical Al/Al cycling with urea-$AlCl_3$ electrolyte and urea-$AlCl_3$ with the addition of toluene (50% w/w).

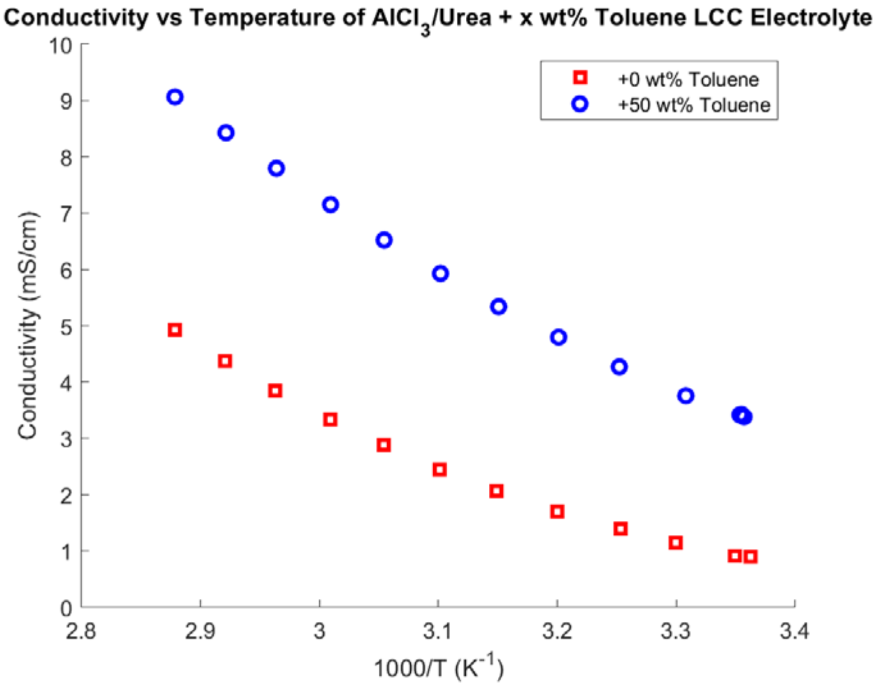
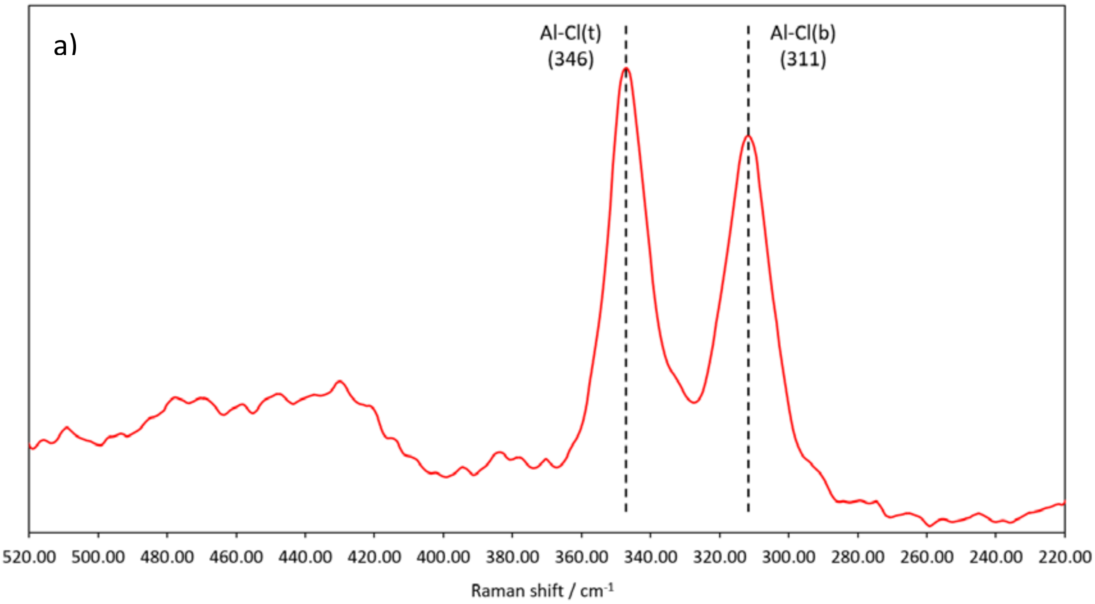


Figure 5 - Conductivity of urea-$AlCl_3$ + wt% toluene.

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).



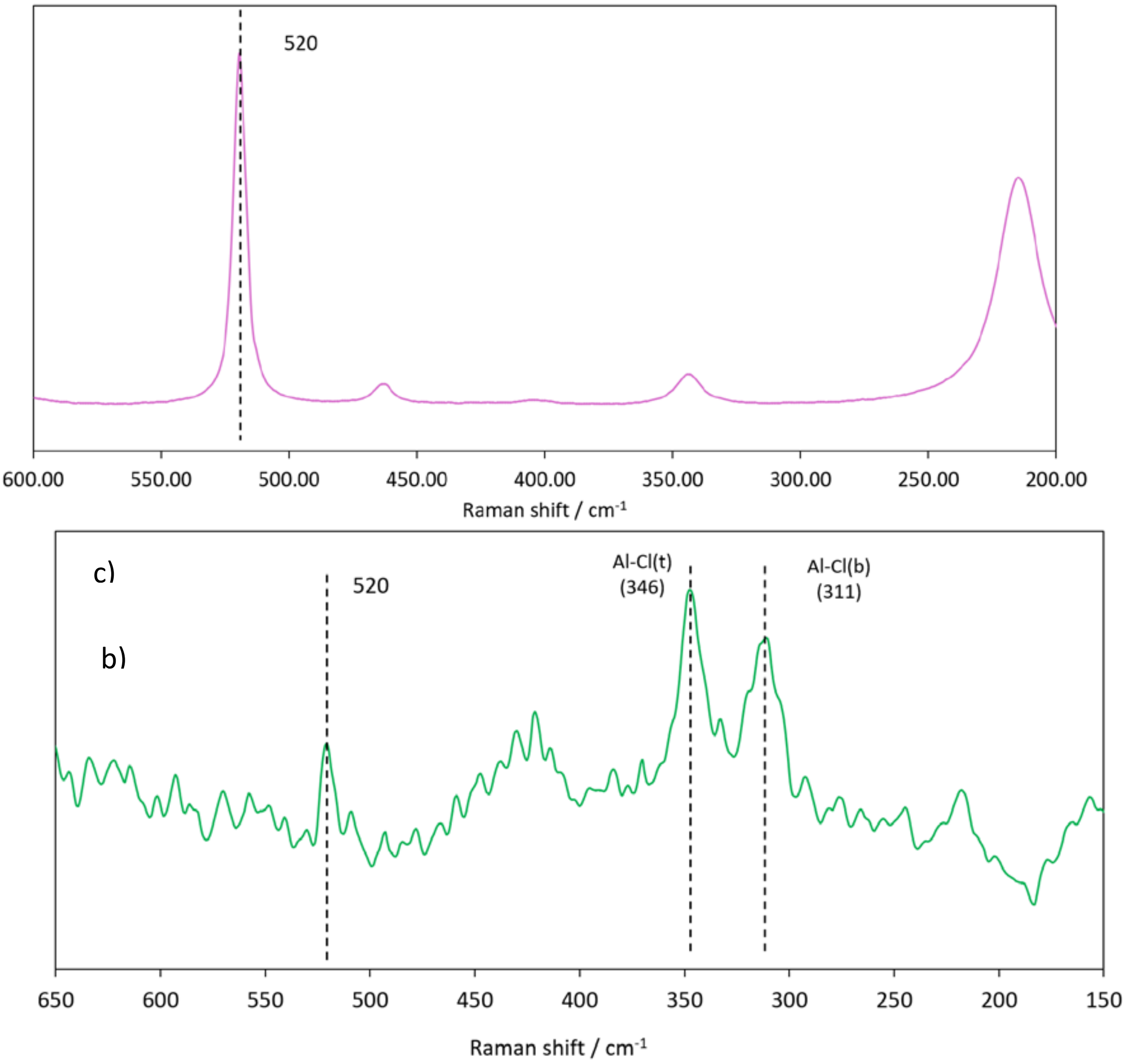


Figure 6 - Raman spectra of a) pure LCC, b) pure toluene and c) LCC + 25% toluene

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.

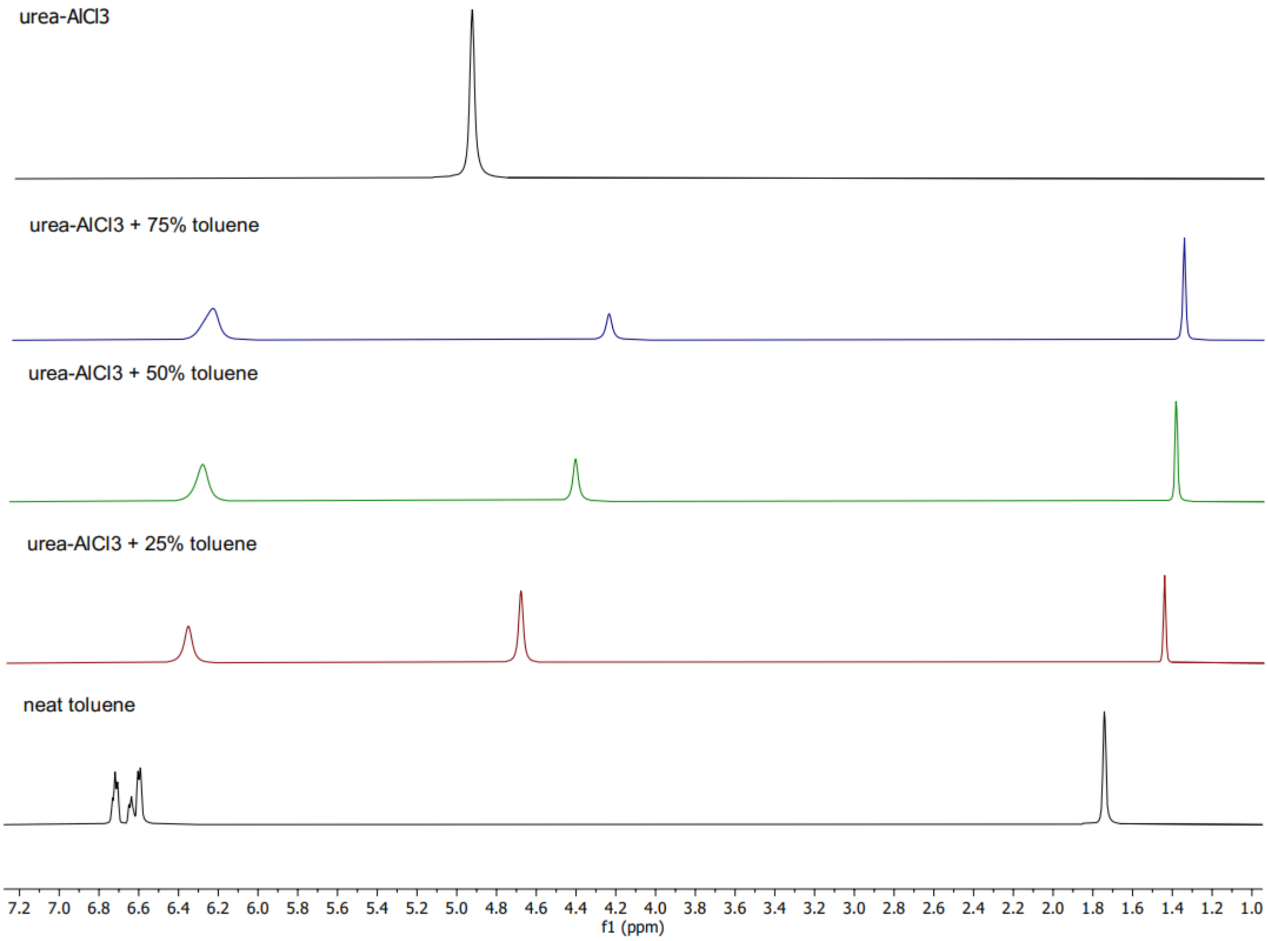


Figure 7 - ^{1}H NMR comparison of urea-$AlCl_3$ with toluene (25%, 50% and 75%) with neat urea-$AlCl_3$ and neat toluene. NMR solvent: d_6-DMSO (capillary).

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.

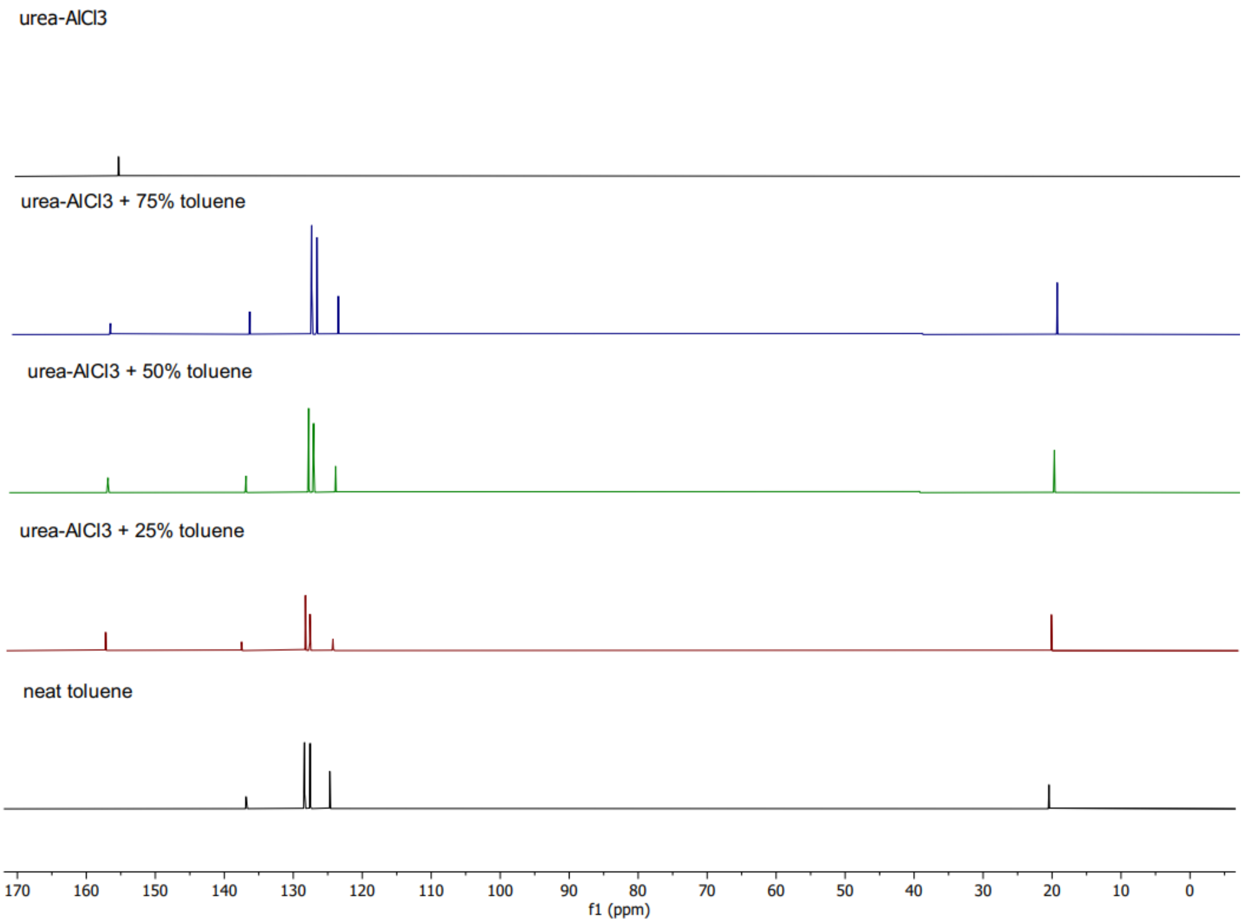


Figure 8 - ^{13}C NMR comparison of urea-$AlCl_3$ with toluene (25%, 50% and 75%) with neat urea-$AlCl_3$ and neat toluene. NMR solvent: d_6-DMSO (capillary).

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.

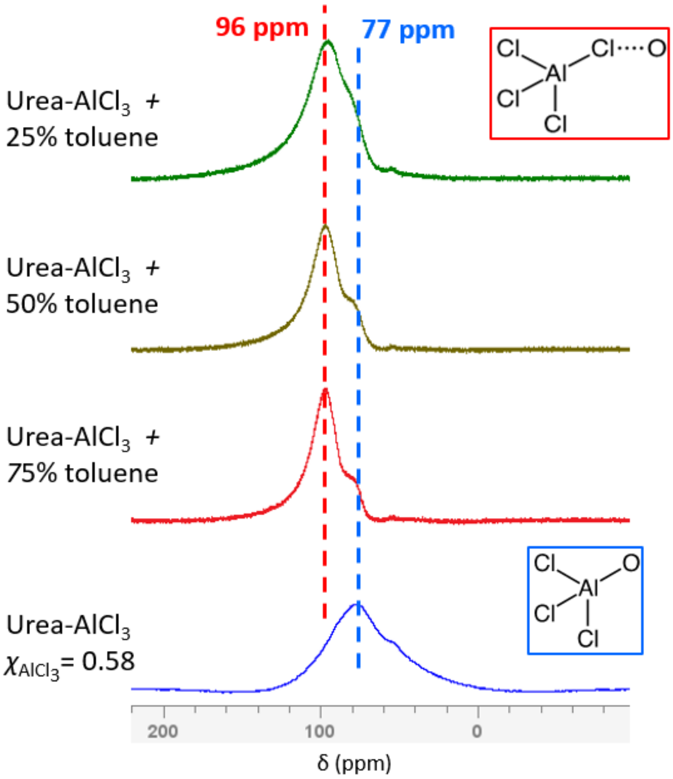


Figure 9 - ^{27}Al NMR comparison of urea-AlCl$_3$ with toluene (25%, 50% and 75%) with neat urea-AlCl$_3$ and neat toluene. NMR solvent: d$_6$-DMSO (capillary).

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.

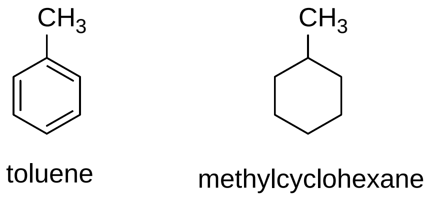


Figure 10 - Chemical structures of toluene and methylcyclohexane

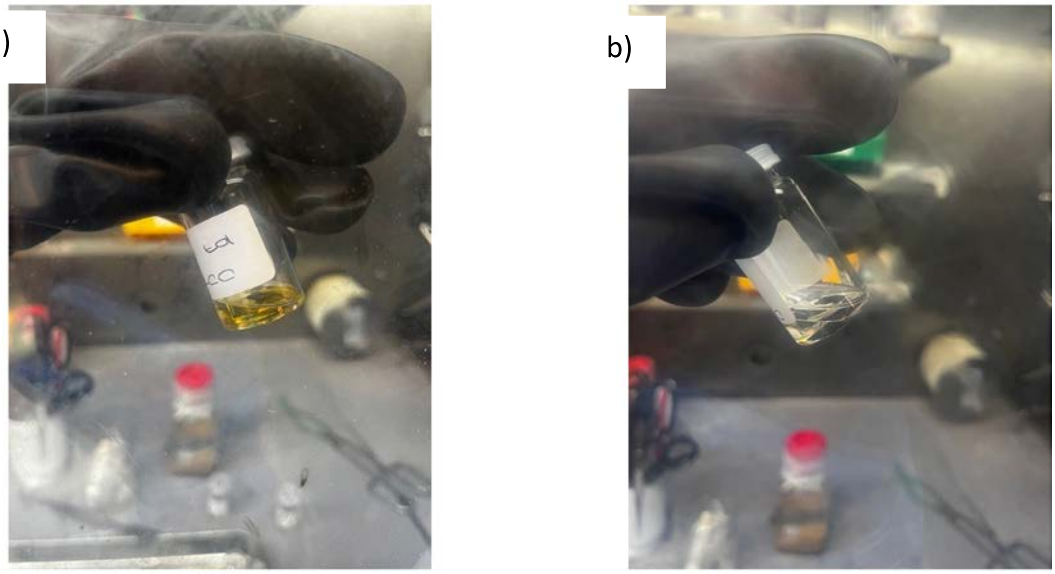


Figure 11 - a) toluene mixed with LCC to form one layer and b) methylcyclohexane mixed with LCC to form two layers

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.

In recent months, I have been working on finishing off experimental studies for this research. This has included using the rolling ball viscometer to measure the viscosities of my samples (neat LCC of urea-$AlCl_3$, and the LCC with toluene). All samples were prepared in a sealed tube inside the glovebox to prevent exposure to atmospheric moisture. Until now I have recorded the viscosity of urea-$AlCl_3$ LCC ($\chi_{AlCl_3} = 0.58$) + 0.96 moles of toluene per Al atom, and urea-$AlCl_3$ ($\chi_{AlCl_3} = 0.58$) + 1.91 moles of toluene per Al atom. The dynamic viscosity (mPa.s) is shown tabulated below (Table 1), with graphs of viscosity *vs.* temperature (K), and log viscosity *vs.* 1/T (Figure 12).

Table 1 - Viscosity of LCC mixtures in the temperature range 293 - 343 K

Sample	**293 K**	**303 K**	**313 K**	**323 K**	**333 K**	**343 K**
Ur-$AlCl_3$ + 0.96 mol toluene	12.06	9.08	7.13	6.11	5.38	4.63
Ur-$AlCl_3$ + 1.91 mol toluene	4.73	3.88	3.19	2.71	2.33	2.10

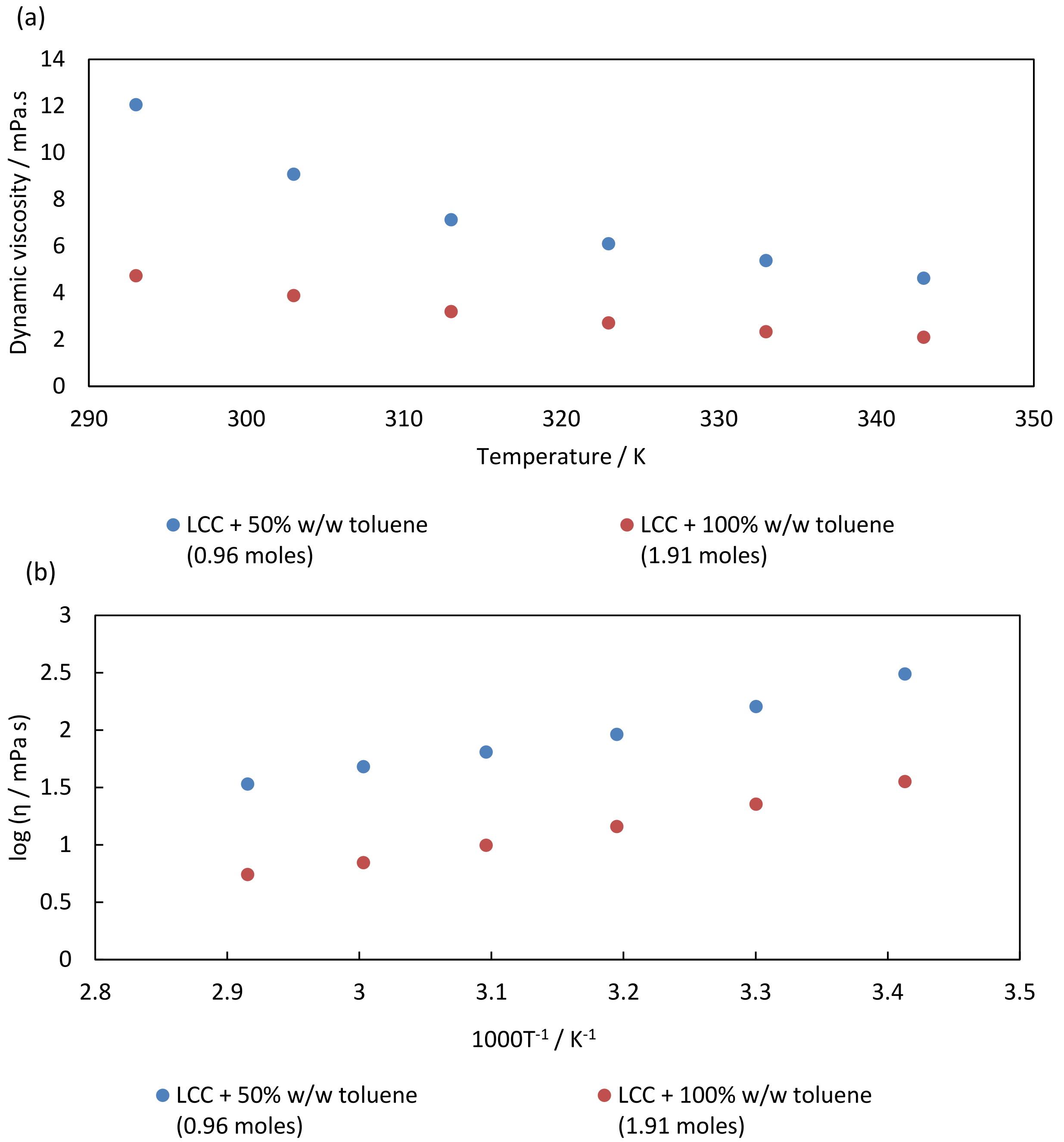


Figure 12 - Graphs of (a) viscosity vs temperature and (b) log viscosity vs 1/T

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 weeks, I plan to finish obtaining the viscosity data for all LCC-toluene compositions, as well as looking to fit the data to a VFT curve. I also plan to finish writing the paper, which will contain all experimental work done so far, and the neutron scattering data from ISIS in October 2024.

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QUILL Quarterly Report

November 2024 – January 2025

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

Implementing Ionic Liquids in PEM Fuel Cell

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) Commissioned the new equipment (Temperature controller, cartridge heaters, mass flow meters).
2) Attempted heating test for the fuel cell. Made modifications to the fuel cell to incorporate cartridge heater and heated the fuel cell successfully to 150 °C with N_2 flowing inside the cell.
3) Evaluated suppliers and in process of ordering new graphite bipolar plates for the fuel cell.

4) Procedure for electrochemically active surface area (ECSA) measurement, and HOR mass activity and surface activity measurement for polycrystalline Pt developed.
5) Ongoing literature review for ink formulation and drying procedure of Pt/C ink over glassy carbon electrode.
6) Ordered longer reference and counter electrodes, and high purity NaOH for more accurate CV (cyclic voltammetry) results.
7) Ordered chemicals, DADMAC and 1-vinylimidazolium for characterisation and synthesis of the first batch of ionic liquids-based proton exchange membranes.
8) COSMOtherm software was explored to estimate solubility between ionic liquids.
9) Submitted initial review report and completed initial review with independent assessor.

Conclusions and future work

1) The fuel cell still seems to have a leak, may need to explore the option of buying a new one which can be sealed reliably.
2) The NaOH which is currently being used might be blocking some active sites on the Pt surface due to impurities. This needs to be confirmed by using high purity NaOH.
3) Solubility tests between poly(ILs), [HVIm][TFSI] and [DADMA][TFSI], and PIL, [Hdema][TfO], to be performed.
4) UV polymerisation of poly(IL) in presence of PIL to be performed.
5) COSMOtherm is better for a qualitative evaluation rather than quantitative evaluation of solubility. A larger dataset needs to be generated to get better understanding of solubility between poly(ILs) and PILs.
6) Pt/C ink with Nafion® and without Nafion® to be deposited on glassy carbon tip and different drying techniques will be evaluated to develop the procedure and formulation which gives the most uniform and thin catalyst layer.
7) To explore the use of gas diffusion electrode cell, which can potentially make the electrochemical studies for catalyst layer more straight forward.

QUILL Quarterly Report

November 2024 – January 2025

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.

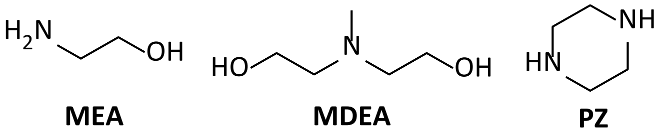

Figure 13 - Structure of common amines used in CO_2 scrubbing

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.

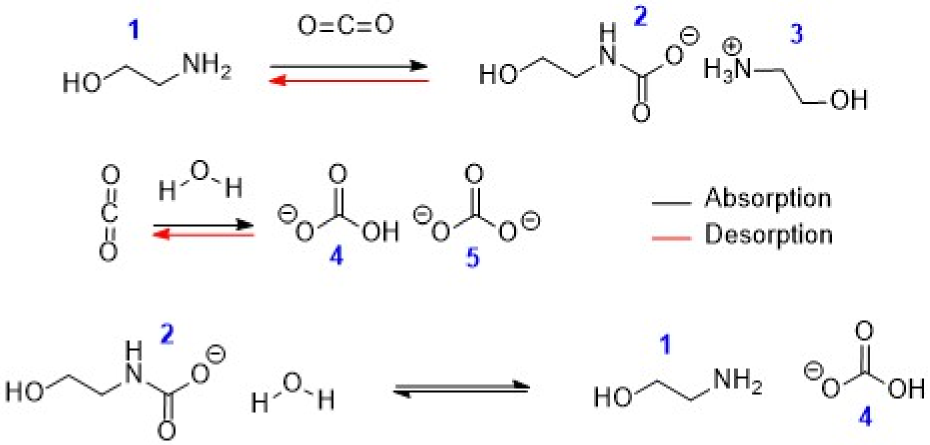

Figure 14 - Reaction pathway for MEA & CO_2

Due to issues with amine scrubbers outlined above a replacement is needed. ILs have the potential to offer such a replacement due to their ease of functionality and potential negligible vapour pressure.

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

- New ILs for high temperature CO2 capture

A new set of imide functionalized anion containing ILs have been shown to have enhanced CO_2 capture properties. Huang et al.[11] showed that preorganization of the imide functionality can enhance CO_2 compared to the unorganized analogue, reporting a CO_2 uptake of 1.25 mol CO_2/mol IL and 1.87 mol CO_2/mol IL when using a $[P_{4442}]^+$ cation and comparing unorganized to preorganized. Structures of the flexible (unorganized) and preorganized anions shown in Figure 3.

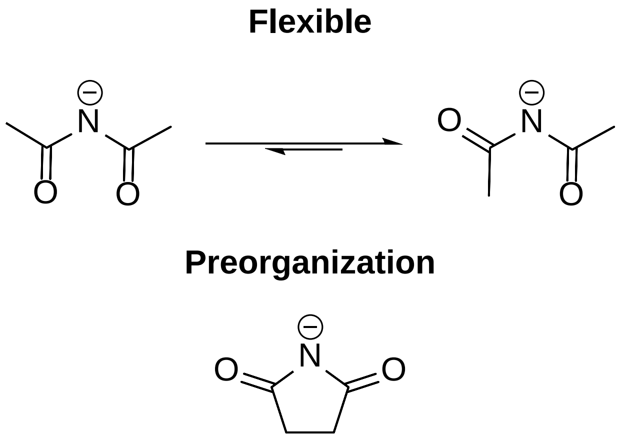

Figure 3 - Top: Diacetamide anion. Bottom: Succinimde anion. Cation for both ILs=$[P_{4442}]^+$

Addition of an electron donating backbone to the succinimide motif also positively influences CO_2 uptake, as can be seen in Figure 4. We proposed further enhancing the electron donating backbone with a range of different anions in an effort to maximise CO_2 absorption.

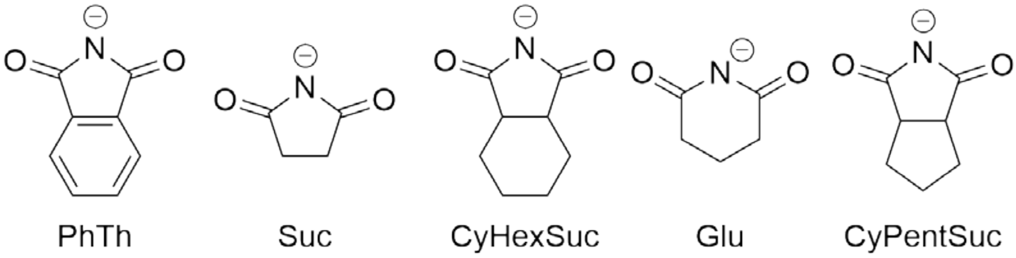

Figure 4 - Imide anion structures. Left to right; phthalimide ($[Phth]^-$), succinimide ($[Suc]^-$), 1,2-cyclohexanedicarboximide ($[CyHexSuc]^-$), glutarimide ($[Glu]^-$), 1,2-cyclopentanedicarboximide ($[CyPentSuc]^-$)

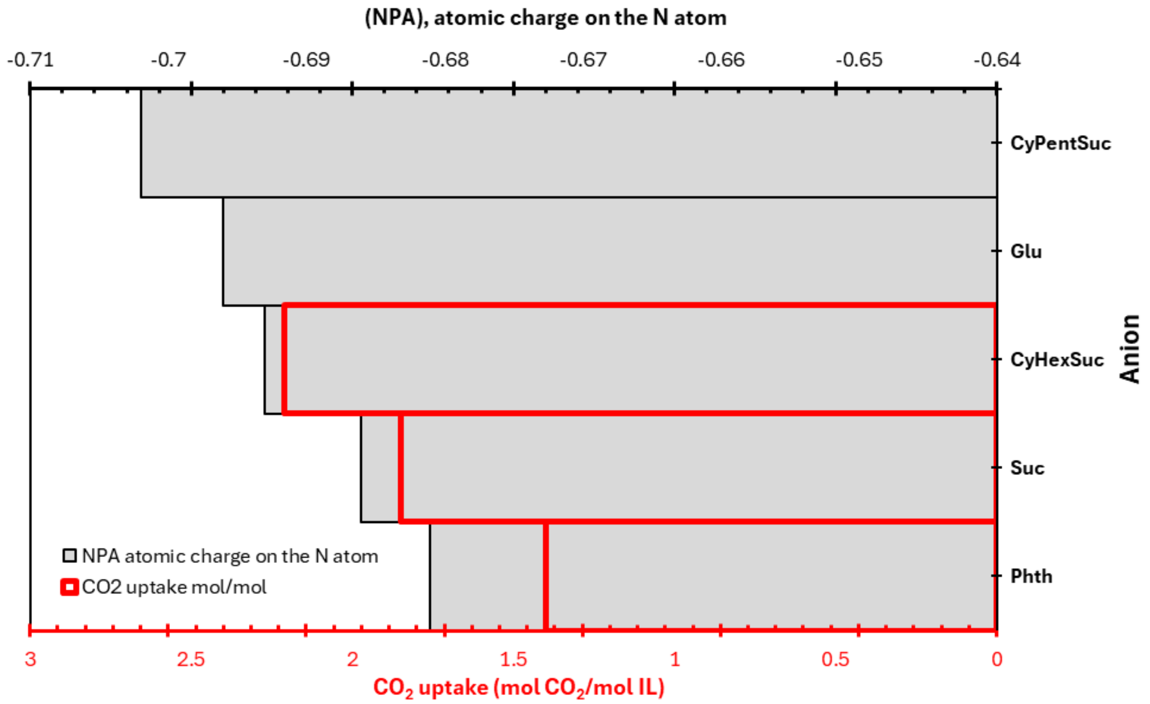

Figure 5 - Bar chart comparing trend of atomic charge and CO_2 uptake. Grey; Natural Population Analysis (NPA) of the atomic charge of the nitrogen atom of the anions, (Fang et al.[12] calculated using B3LYP/6-31++G(p,d).). Red; reported CO_2 uptake of the anions (Cation = $[P_{4442}]$)[13]. No reported literature for CO_2 uptake with $[CyPentSuc]^-$ and $[Glu]^-$ anions.

However during the synthesis of the succinimide based ILs we found that the anion is susceptible to hydrolysis in the presence of water (Figure 6.) evident by two new peaks in the ^{13}C NMR at ~175 ppm, this hydrolysis can be seen in the literature NMR but is not thoroughly discuss. Therefore we proposed a new synthesis route that allows for the synthesis of these anions. (Figure 7.)

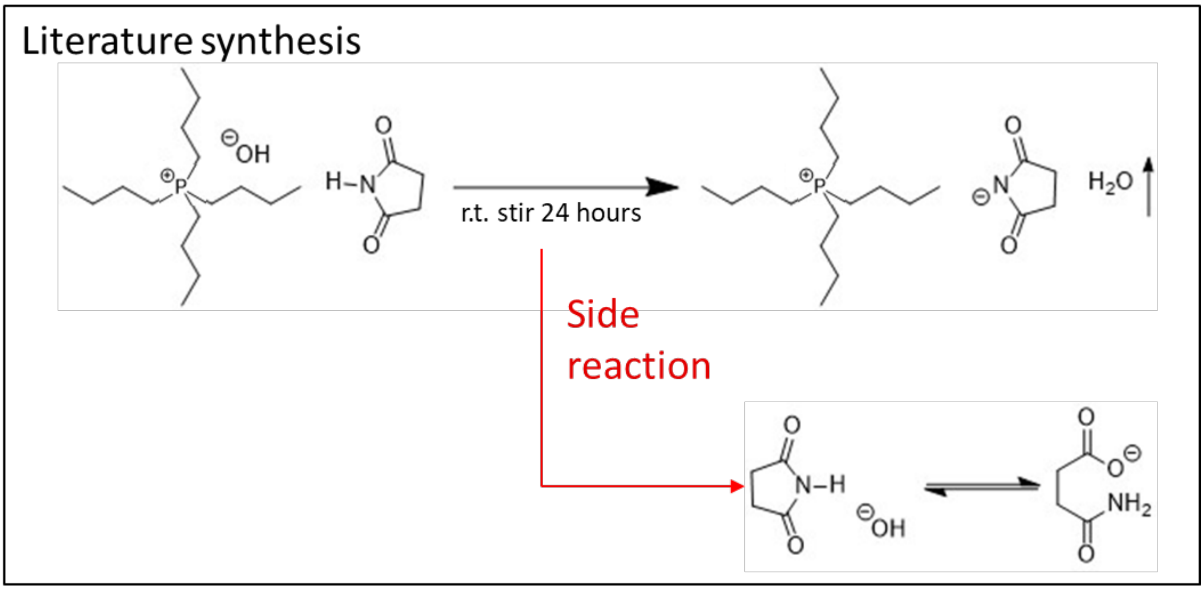

Figure 6 - Synthesis route reported in the literature using a hydroxide precursor in 40 wt% ethanol solution. Bottom: Hydrolysis of the imide motif.

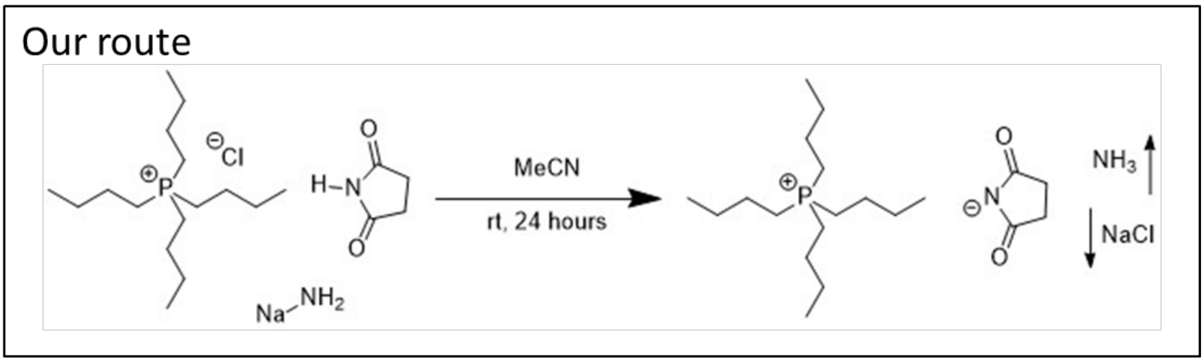

Figure 7 - New synthesis route that eliminates the potential for imide hydrolysis.

Interestingly we also found that the succinimide based anions can be thermally dehydrated after the ring has opened however this can cause the cation to degrade by forming a ylide evidence through multiple peaks in the ^{31}P NMR. This dehydration was only evident in the $[P_{4444}]^+$ cation containing ILs and not the tetrabutylammonium ($[N_{4444}]^+$) based ILs as with the ILs that utilized a $[N_{4444}]^+$ cation, decomposition of the IL had already begun (Blue line Figure 8.). For $[P_{4444}]$[CyHexSuc] (Figure 8, Green line) there is a mass loss of ~4 wt% the corresponding wt% of water in the IL is 4.18%. This was confirmed by NMR which show a removal of the hydrolysis product peaks and a single carbonyl peak at ~192 ppm indicative of the desired anion structure.

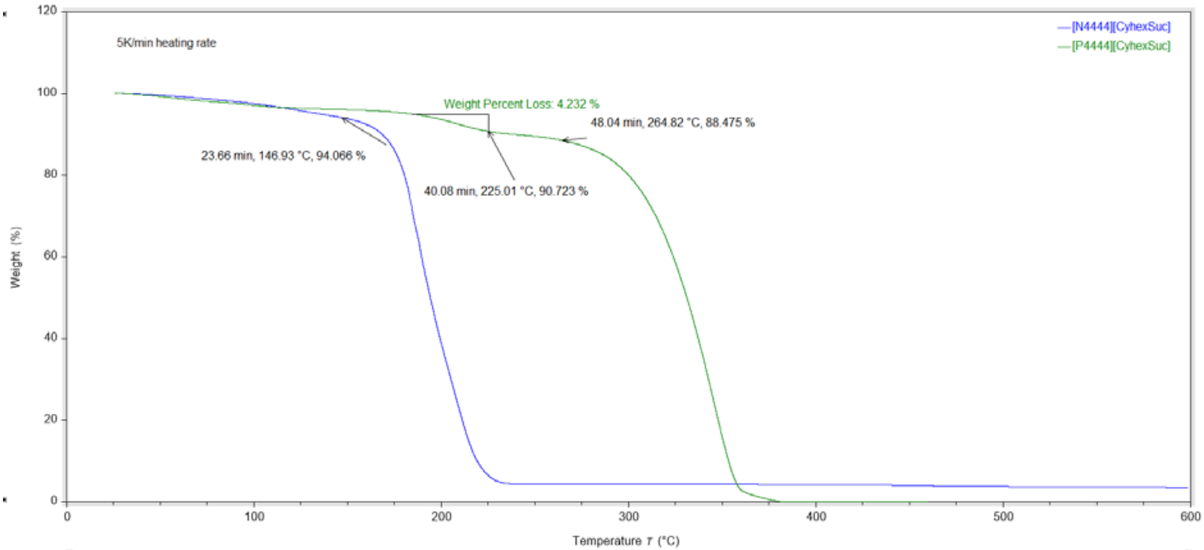

Figure 8 - TGA curve for dehydration of the hydrolysis succinimide ILs 5K/min. Blue line: $[N_{4444}]$[CyHexSuc]. Green line: $[P_{4444}]$[CyHexSuc].

Using a thermally stable cation would allow for this dehydration of the succinimide anion and thus IL recyclability especially in terms of CO_2 uptake from wet gas streams. We investigated a thermally stable cation, tetraphenylphosphonium ($[P(Ph)_4]^+$) used in the IL tetraphenylphosphonium bistriflimide ($[P(Ph)_4][NTf_2]$) reported by Davis et al.[14] which can be held at 350 °C for 96 hours and reported only a 0.8 wt% loss. However the $[P(Ph)_4]^+$ cation is unstable in a basic environment which can be seen in the ^{31}P NMR. The degradation products are still being determined. All phosphorus starting materials have only one peak in the ^{31}P NMR. Work is now underway to find a thermally stable and base stable cation.

Conclusions and future work

Succinimide based anions offer the potential for enhanced CO_2 capture however the correct cation for the IL is imperative for it to IL to be stable. Ongoing work to determine the CO_2 uptake for this ILs.

Work is underway to find a base stable cation which can allow for the dehydration of the succinimide anion to occur unhindered. Potential cations that have shown to be thermally stable and stable under basic conditions.

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QUILL Quarterly Report

November 2024 – January 2025

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 New Borates Anion

Background

Ionic liquids containing boron-based anions have a long and varied history, from tetraalkylammonium tetraalkyl borides, in 1970, tetrahexylammonium benzoate was used as a solvent for electrochemistry and kinetic studies and the polarity of tetrahexylammonium benzoate was estimated to lie between those of ethanol and water.[1] [2]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 solid electrolyte interphases (SEI) where SEI, electrically insulating and ionically conductive passivation layer which is formed on the electrode surface through electrolyte decomposition, plays an important role in the determination of Coulombic efficiency, cycle life, capacity, and safety.[3]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. 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

Recent work in QUILL (H Amir, PhD thesis, 2024) has shown that N/O-chelated borate anions can be developed and used as ionic liquid electrolytes and electrolyte additives for battery applications, and that the inclusion of N-coordinated ligands on boron in these anions results in enhancement of stability compared to labile B-O coordinated analogues such as glycerol-borates. 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. At this point (for the APR that will come this year) the objectives with borate anions are to explore the potential to use N/O- and N/Nchelating 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 voltammetry 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.

Deprotonation of Alkanolamine

Sodium bicarbonate ($NaHCO_3$) deprotonates the hydroxyl group (–OH) of the alkanolamine, generating a sodium alkoxide intermediate with the removal of water and carbon dioxide.

$$\mathbf{R\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}OH + NaHCO_3 \rightarrow R\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2O^-Na^+ + H_2O + CO_2}$$

Formation of Borate Anion

The alkoxide reacts with boric acid ($B(OH)_3$) to form a borate anion chelated by the nitrogen (N) and oxygen (O) atoms of the alkanolamine.

$$\mathbf{2R\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}O^- + B(OH)_3 \rightarrow [R\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}O\text{-}B\text{-}O\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}R]^- + 3H_2O}$$

Solvent and Reflux

Toluene is used as the solvent to remove water (azeotropic distillation) and drive the reaction to completion. Reflux ensures efficient mixing and reaction progress

Progress to date

Literature review related to the sodium borates starting from the contribution of Wilkes 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. Initially, replicating the synthesis from Haris' thesis and then extending this to the series of N-substituted alkanolamines which have not previously been reported

- Skill training on Glove Box, NMR, DSC, and rotatory evaporator.
- Visited ISIS for learning Neutron Scattering with Kerri McKeever and Beth Murray under the supervision of Prof. Gosia Swadzba-Kwasny.
- Prepared a sodium borate salt using 2-benzylamino ethanol and performed $^1H/^{11}B/^{13}C$ NMR where D_2O was used as solvent

Table 1 - Synthesis of borate anion
(**Red** = Planned, **Green** = In progress, **Amber** = performed but failed)

Alkanolamine Derivative	**Reagents (Molar Ratio)**	**Solvent**	**Expected Borate Anion**	**Progress**
2-Methyl-ethanolamine	$NaHCO_3$: $B(OH)_3$: Alkanolamine (1:1:2)	Toluene	[Me-N/O-B-O/N-Me]$^-$	🟢
2-Ethyl-ethanolamine	$NaHCO_3$: $B(OH)_3$: Alkanolamine (1:1:2)	Toluene	[Et-N/O-B-O/N-Et]$^-$	🔴
2-Butyl-ethanolamine	$NaHCO_3$: $B(OH)_3$: Alkanolamine (1:1:2)	Toluene	[Bu-N/O-B-O/N-Bu]$^-$	🔴
2-Benyl-ethanolamine	$NaHCO_3$: $B(OH)_3$: Alkanolamine (1:1:2)	Toluene	[Bn-N/O-B-O/N-Bn]$^-$	🟡

Conclusions and future work

Synthesis of remaining 11 sodium borate anions and to generate a matrix of ionic liquids/organic salts from these anions by cation exchange still need to be done. The potential cation could be used will be tetrabutylphosphonium ([P4444]+), 1-butyl-3-methylimidazolium ([C4mim]+) and ethylmethylpyrrolidinium (C2C1pyrr]+).

Table 2 -Preparation of tetrabutylphosphonium, 1-butyl-3-methylimidazolium, ethylmethylpyrrolidinium ILs

Ethanolamine Derivative	**Cation**	**Expected Salt**	**Salt Abbreviation**
2-Methyl-ethanolamine	$[P_{4444}]^+$	$[P_{4444}][B(C_3H_7NO)_2]$	$[P_{4444}]$[Me-Borate]
2-Methyl-ethanolamine	$[C_4mim]^+$	$[C_4mim][B(C_3H_7NO)_2]$	$[C_4mim]$[Me-Borate]
2-Methyl-ethanolamine	$[C_2C_1pyrr]^+$	$[C_2C_1pyrr][B(C_3H_7NO)_2]$	$[C_2C_1pyrr]$[Me-Borate]
2-Ethyl-ethanolamine	$[P_{4444}]^+$	$[P_{4444}][[B(C_4H_9NO)_2]$	$[P_{4444}]$[Et-Borate]
2-Ethyl-ethanolamine	$[C_4mim]^+$	$[C_4mim][B(C_4H_9NO)_2]$	$[C_4mim]$[Et-Borate]
2-Ethyl-ethanolamine	$[C_2C_1pyrr]^+$	$[C_2C_1pyrr][B(C_4H_9NO)_2]$	$[C_2C_1pyrr]$[Et-Borate]
2-Butyl-ethanolamine	$[P_{4444}]^+$	$[P_{4444}][B(C_6H_{13}NO)_2]$	$[P_{4444}]$[Bu-Borate]
2-Butyl-ethanolamine	$[C_4mim]^+$	$[C_4mim][B(C_6H_{13}NO)_2]$	$[C_4mim]$[Bu-Borate]
2-Butyl-ethanolamine	$[C_2C_1pyrr]^+$	$[C_2C_1pyrr][B(C_6H_{13}NO)_2]$	$[C_2C_1pyrr]$[Bu-Borate]
2-Benzyl-ethanolamine	$[P_{4444}]^+$	$[P_{4444}][B(C_9H_{11}NO)_2]$	$[P_{4444}]$[Bn-Borate]
2-Benzyl-ethanolamine	$[C_4mim]^+$	$[C_4mim][\ B(C_9H_{11}NO)_2]$	$[C_4mim]$[Bn-Borate]
2-Benzyl-ethanolamine	$[C_2C_1pyrr]^+$	$[C_2C_1pyrr][B(C_9H_{11}NO)_2]$	$[C_2C_1pyrr]$[Bn-Borate]

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QUILL Quarterly Report

November 2024 – January 2025

Name:	Jamie Warren		
Supervisor(s):	Prof Gosia Swadźba-Kwaśny		
Position:	PhD Student		
Start date:	October 2024	**Anticipated end date:**	April 2028
Funding body:	EPSRC/Ionic Technologies		

Hydrometallurgical Separation of Adjacent Rare Earth Elements in an NdFeB Magnet Recycling Process

Background

Rare Earth Elements (REEs) are becoming increasingly important in the transition towards Net Zero. These metals see use in various high-tech applications, for example, in wind turbine generators, electric vehicle (EV) batteries, and compact fluorescent lamps. Owing to their minerals being found in geographically isolated locales, the supply of REEs worldwide poses numerous challenges: a small number of countries (*e.g.* China, USA *etc.*) have the means to directly mine REEs and therefore can restrict their export to other regions of the globe where demand is high. Additionally, the mining of REEs from their ores is environmentally non-sustainable, so it is therefore important to develop other strategies for securing the supply of these elements.

In order to mitigate the supply risk of REEs globally, recycling has been proposed as a viable strategy: the metals can be taken from end-of-life (EoL) products such as spent permanent magnets and separated to generate high purity individual metals for further use. This is typically achieved industrially through solvent extraction processes, which is a subset of hydrometallurgy. In solvent extraction, metal ions dissolved in an aqueous solution are contacted with an immiscible non-polar organic phase containing an extracting ligand. This enables separation of metals based on different binding affinities for the ligand; however, it should be noted that due to their very similar ionic radii and coordination behaviour, adjacent REE ions are very difficult to separate efficiently, with many hundreds of extraction stages often required to produce individual metals in sufficiently high purity for reuse. Solvent extraction processes are also reagent intensive and lead to the generation of large amounts of waste which is environmentally harmful.

Objective of this work

This PhD project aims to improve the separation of the adjacent heavy REEs, Dy and Tb, within a scalable and commercially viable NdFeB permanent magnet recycling process. This is to be achieved through investigation of various parameters, including the use of X-ray absorption spectroscopy (*e.g.* EXAFS, XANES *etc.*) to elucidate the fundamental molecular phenomena underpinning the metal extraction process.

Progress to date

To date, lab scale benchmark extraction experiments have been carried out for both Dy and Tb using the commercial extractants, P507 and Cyanex 272, as well as investigating the effect of an ionic liquid additive ([A336][P507]) on extraction performance.

A 3-day visit to the Diamond Light Source in Didcot, Oxford has been carried out to receive training in sample preparation and data analysis for X-ray absorption spectroscopy (EXAFS).

Conclusions and future work

In order to gain insight into the relationship between the coordination environment of the extracted metal complexes and the observed extraction/separation performance of the ligand used, it is necessary to generate an extensive data matrix for the benchmark and novel systems under study to enable comparison to any spectroscopic data generated for the extracted metals.

In addition to investigating the use of ionic liquid additives on Dy/Tb extraction performance, hydrophobic deep-eutectic solvents (DESs) can also be used as novel extractant media in REE solvent extraction processes. As there is currently a dearth of literature probing hydrophobic DESs in REE separation, this is a worthwhile avenue to explore as part of this PhD project.

QUILL Quarterly Report

November 2024 - January 2025

Name:	Anna White		
Supervisor(s):	Dr Paul Kavanagh and Dr Leila Moura		
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. Building on this, water-in-salt electrolytes based on the quaternary ammonium salts used for deep eutectic solvents present interesting properties for use as electrolytes.

The electrochemical reduction of CO_2, especially using aqueous electrolytes, 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 different aqueous electrolytes 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.

Our initial study into aqueous quaternary ammonium salt electrolytes includes physical characterisation by FTIR spectroscopy, viscosity measurements and NMR spectroscopy. Following this, in-depth electrochemical characterisation has been conducted.

The physical characterisation by FTIR-spectroscopy have allowed deeper understanding of the interactions occurring between the quaternary ammonium salts and water within the solvents. Viscosity measurements were conducted as viscosity can greatly impact the efficiency of an electrolyte due to the mass transport phenomenon.

The electrochemical stability windows (ESW) of the electrolytes were investigated to determine the effect of increasing salt concentration on the stability of water during electrochemical processes. We found that on less catalytically active working electrodes, for example glassy carbon and boron-doped diamond, the ESW of the solvents increased on increasing solute concentration, to as wide as 3.4 V. However, on more catalytically active surfaces such as gold and platinum, this was not observed.

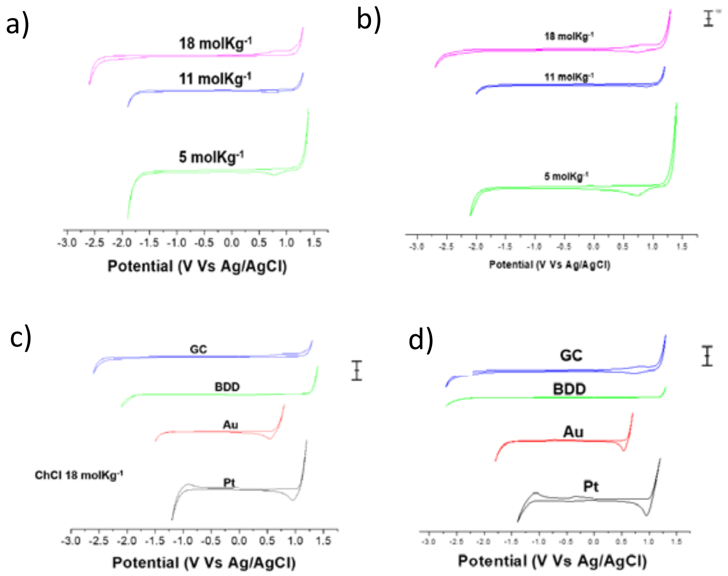

Figure 1 - a) and **b)** Electrochemical stability windows of choline chloride electrolytes and tetramethylammonium chloride electrolytes and different concentrations on a glassy carbon electrode, respectively. C) and d) ESWs of 18 molKg^{-1} aqueous solutions of ChCl and TMAC, respectively, at different working electrode surfaces.

Following this, further electrochemical characterisation of the electrolytes was conducted by introducing ferricyanide as a redox probe. Cyclic voltammetry studies of the 5 mM ferricyanide solutions showed that, as solute concentration increases, the redox potential of the electrolytes decreases for both ChCl and TMAC electrolytes.

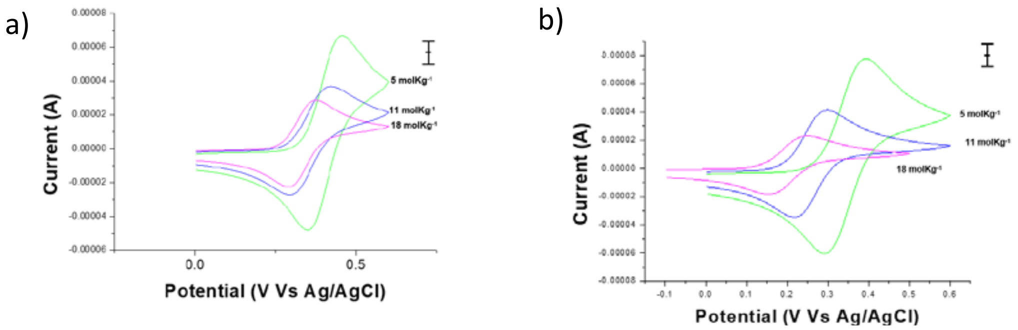

Figure 2 - Cyclic voltammograms of 5 mM ferricyanide in a) ChCl and b) TMAC at different concentrations

Rotating disk voltametric studies were also conducted to determine the diffusion coefficient and the electron transfer constant of the various electrolytes. These results can be summarised in the table below.

Solvent	E°	K°	D
ChCl 5M	0.395671	0.007277	9.08E-07
ChCl 11M	0.347575	0.003976	2.54E-07
ChCl 18M	0.322592	0.012915	9.38E-08
TMAC 5M	0.340497	0.00751	1.10E-06
TMAC 11M	0.263834	0.005957	2.46E-07
TMAC 18M	0.134782	0.001829	1.05E-07

Table 1 - Summary of electrochemical properties of aqueous choline chloride and tetramethylammonium chloride electrolytes.

Conclusions and future work

Initial electrochemical characterisation of the studied aqueous ammonium salt electrolytes presents interesting electrochemical properties. Future work will involve introduction of different redox probes such as quinones into the solvents for analysis. Quinones are of specific interest as they have been used in past work for the capture and release of carbon dioxide. The above findings also indicate the possible use of these electrolytes for other electrochemical processes, such as flow cell batteries. We will further investigate the practical application of using these electrolytes for such purposes.