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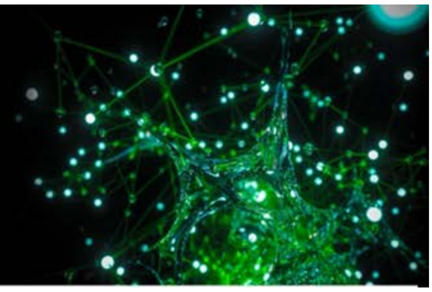

QUILL
Quarterly Reports

August - October 2023

CONFIDENTIAL (up to November 2026)

Contents

QUILL Quarterly Report

August 2023 – October 2023

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

Design of New, Non-Coordinating, and Hydrophobic Anions for Functional Ionic Liquids

Background

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

These borate salts were then investigated as halogen free electrolytes for sodium ion batteries. This was done by preparing coin cells and running electrochemical analysis such as, cyclic voltammetry, Scanning electron microscopy paired energy dispersive x-ray. SEM paired with EDX was chosen to better understand how the borate salts are electrochemically degrading and if they are forming a solid electrolyte interphase (SEI) . The following work was carried conducted during a visit to Deakin university, Institute for Frontier Materials (IFM) under the supervision of Professor Maria Forsyth and Dr. Mega Kar.

Electrochemical studies

Figure 1 shows a schematic diagram of the preparation of a coin cell, the anode was chosen to be sodium metal, while the cathode was copper foil. Copper was chosen as it is highly sensitive to any plating/stripping occurring during the redox of sodium. This can then be easily picked up in CV graphs.

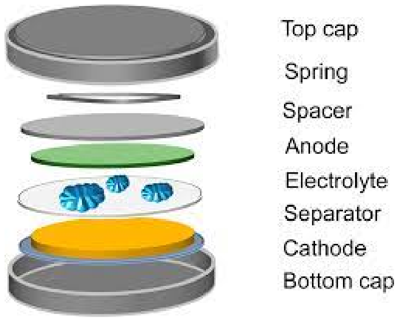

Figure 1 - Schematic diagram of a coin cell

The borate salts where first dissolved in dimethoxyethane (DME) and then added as illustrated in figure 1. The oxidation and reduction of four sodium borate salts are shown in figure 2 and 3 respectively. The oxidation of the sodium borate salts showed no oxidation of sodium but does show deposition and breakdown of the electrolyte. The reduction of the sodium borates also showed no reduction of sodium and only showed the breakdown of the borate salts.

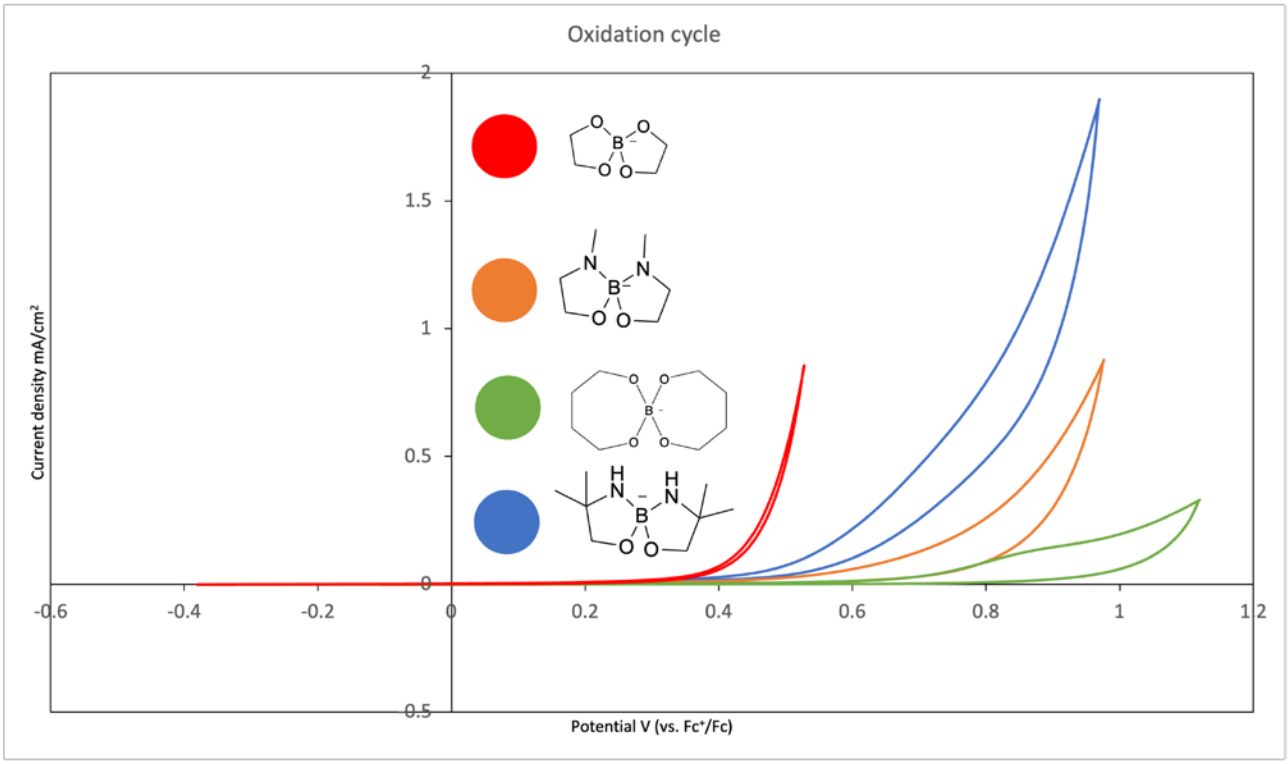

Figure 2 - Oxidation cycle of sodium borate salts

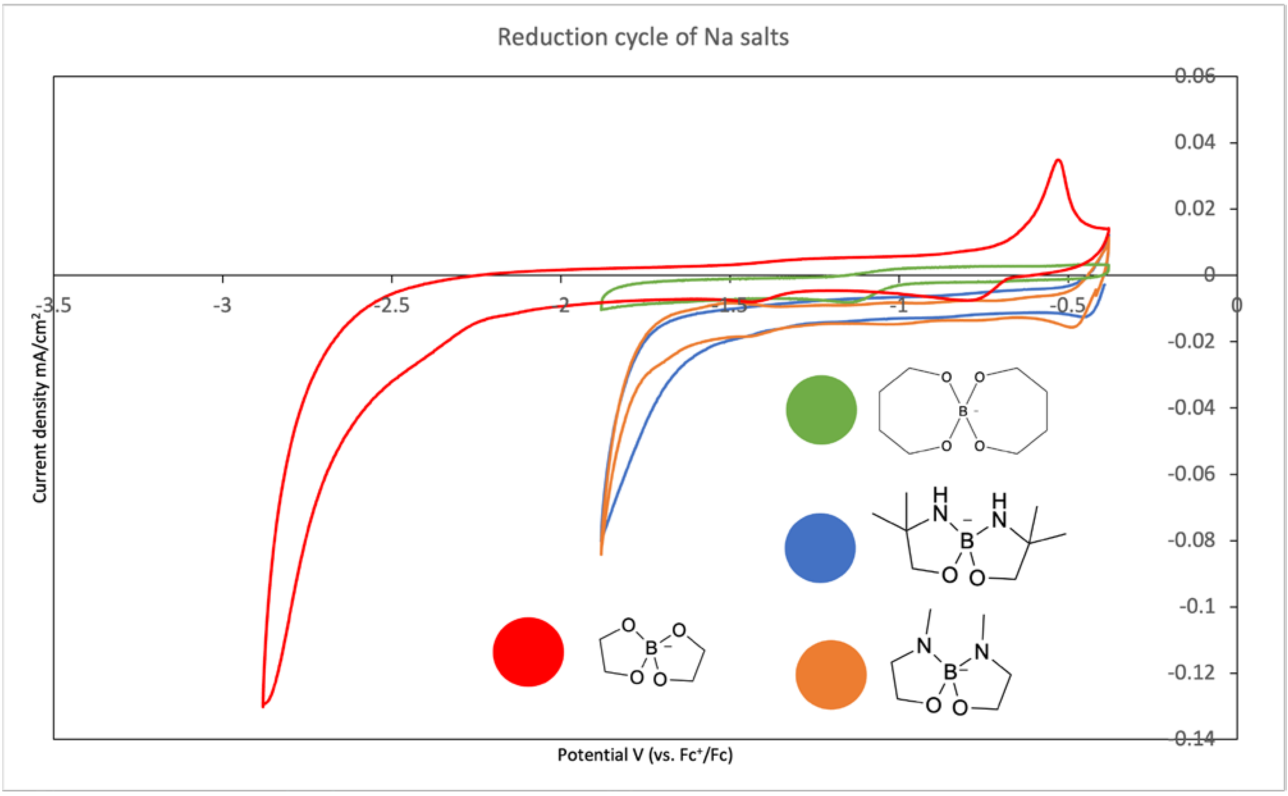

Figure 3 - Reduction cycle of sodium borate salts

Once it was determined that the borate salts are not performing as intended it was then investigated it the breakdown of these borates are forming favourable SEI layers. This was done by disassembling the coin cell and carrying out SEM and EDX analysis of the anode and cathode. Figure 4 shows the sodium anode for $Na[B(C_3H_7NO)_2]$, the anode shows clear layer of chemical deposition. When carrying out EDX analysis it was found that the centre 'lumps' where a mixture of carbon (10 %) and oxygen (35 %) surrounding this mixture was sodium (55 %). Unexpectedly there was no signs of nitrogen deposition on the sodium anode, while boron was to light to be seen using EDX. Figure 5 shows the copper cathode of $Na[B(C_3H_7NO)_2]$, the cathode showed a far more interesting picture. The SEM showed a porous like structure in the centre, when carrying out EDX analysis it was found that the porous structure was largely from nitrogen (7 %), Oxygen (18 %), carbon (8 %) and sodium (9 %). The surrounding was copper (58 %), it is difficult to determine if the 9 % sodium plating on the copper cathode is from the sodium metal anode or from the sodium salt electrolyte decomposing. Despite this uncertainty the SEM show clear formation of an SEI layer. Future work will be to investigate how effective the SEI layer formed is, this will be done by using the borate salts as sacrificial electrolytes in order to form an SEI layer and see how the sodium coin cell perform with the formation of this SEI layer.

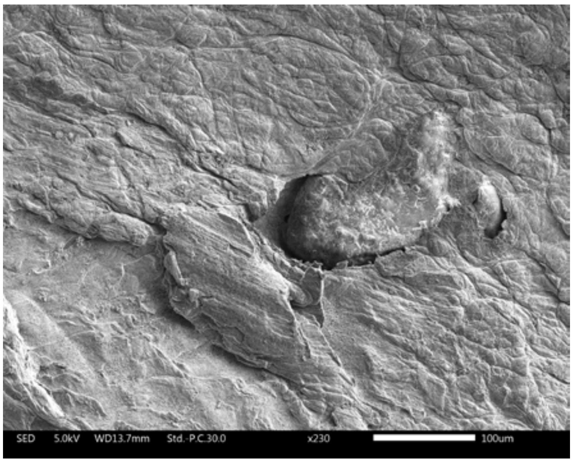

Figure 4 - SEM of the sodium anode for $Na[B(C_3H_7NO)_2]$ coin cell

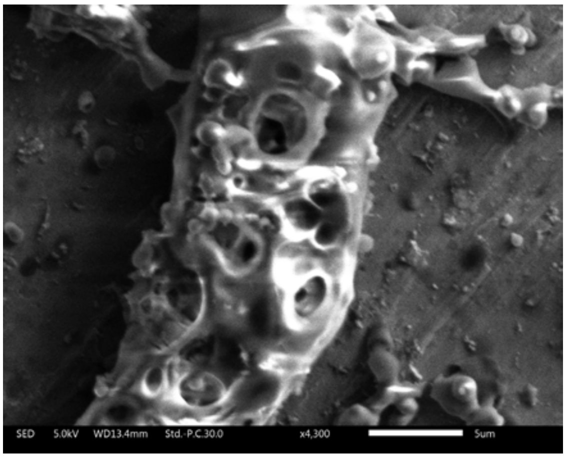

Figure 5 - SEM of the copper cathode for $Na[B(C_3H_7NO)_2]$ coin cell

QUILL Quarterly Report

August 2023 – October 2023

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

The following post-graduate training programmes have been completed:
- "How to read critically and take good notes" by Fabiana McCracken at Queen’s University.
-"Training on Pure and the Research Portal " by Rebecca Clarke at Queen’s University.

- Academic writing courses by Rachael O'Neill at Queen’s University (8 weeks).

A literature review was completed and presented to Prof. Nockemann.
Structure of the literature review:

1. Ionic liquids
2. Ionic liquids for inorganic synthesis
3. Molecular magnets
4. Synthesis of Molecular Magnets
5. Ionic liquids for the synthesis of MMs
6. Magnetic Ionic Liquids (MILs)
7. Characterisation of MMs

Conclusions and future work

Slide presentations and posters were prepared and presented for the QUILL meeting held in October. The part of the project for this term consists of three main synthesis and characterisation stages, and synthesis and various characterisations have been completed for the first and second steps.

Experiments are continuing for the synthesis of the final material, boron containing rare-earth molecular magnet.

QUILL Quarterly Report

August 2023 – October 2023

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

Parametric Study of Electrolyte Flow in 3D-Printed Operando Redox Flow Cells

Overview

The aim of this project is to improve the electrochemical activity of redox flow batteries through electrode/electrolyte interaction enhancement. This is achieved through using novel techniques to improve otherwise limiting factors in certain systems such as poor electrode wettability (due to the hydrophobic nature of carbon) and electrochemically active surface area (ECSA). In improving the electrochemical capability of such systems, redox flow battery technology could be a viable alternative to large scale traditional renewable energy storage.

Work to date

The main objective of my work to date has been to become familiar with literature relevant to my topic along with the techniques that could be applied to my own experiments, including two PowerPoint presentation on the following papers:

Presentation Friday 20th October 2023

1. Boric acid thermal etching graphite felt as a high-performance electrode for iron-chromium redox flow battery.(1)

2. Graphene-Nanowall-Decorated Carbon Felt with Excellent Electrochemical Activity Toward VO2+/VO2+ Couple for All Vanadium Redox Flow Battery.(2)

3. A novel approach for forming carbon nanorods on the surface of carbon felt electrode by catalytic etching for high-performance vanadium redox flow battery.(3)

Presentation Thursday 9th November 2023

1. Enhanced electrochemical activity of carbon felt for V2+/V3+ redox reaction via combining KOH-etched pretreatment with uniform deposition of Bi nanoparticles.(4)

2. Boron-functionalized carbon felt electrode for enhancing the electrochemical performance of vanadium redox flow batteries.(5)

3. Taurine Electrografting onto Porous Electrodes Improves Redox Flow Battery Performance.(6)

Initial Workplan

Through reviewing literature as detailed above, several potential directions for initial research have been identified. These include the study of system specific nanomaterials for electrode enhancement, amino acid as potential electrocatalysts, system enhancement lifespan analysis and a combination of previously reported techniques such as combining etching techniques with suitable nanomaterial deposition. The first stage of exploring these avenues is developing a COSHH assessment and completing safety training before entering the lab, which is expected to begin week commencing 13/11/2023.

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1. Li Z, Guo L, Chen N, Su Y, Wang X. Boric acid thermal etching graphite felt as a high-performance electrode for iron-chromium redox flow battery. Materials Research Express. 2022;9:025601.
2. Li W, Zhang Z, Tang Y, Bian H, Ng T-W, Zhang W, et al. Graphene-Nanowall-Decorated Carbon Felt with Excellent Electrochemical Activity Toward VO2+/VO2+ Couple for All Vanadium Redox Flow Battery. Advanced Science. 2016;3(4):1500276.
3. Abbas S, Lee H, Hwang J, Mehmood A, Shin H-J, Mehboob S, et al. A novel approach for forming carbon nanorods on the surface of carbon felt electrode by catalytic etching for high-performance vanadium redox flow battery. Carbon. 2018;128:31-7.
4. Lv Y, Zhang J, Lv Z, Wu C, Liu Y, Wang H, et al. Enhanced electrochemical activity of carbon felt for V2+/V3+ redox reaction via combining KOH-etched pretreatment with uniform deposition of Bi nanoparticles. Electrochimica Acta. 2017;253:78-84.
5. Park SE, Yang SY, Kim KJ. Boron-functionalized carbon felt electrode for enhancing the electrochemical performance of vanadium redox flow batteries. Applied Surface Science. 2021;546:148941.
6. Boz EB, Boillat P, Forner-Cuenca A. Taurine Electrografting onto Porous Electrodes Improves Redox Flow Battery Performance. ACS Applied Materials & Interfaces. 2022;14(37):41883-95.

QUILL Quarterly Report

August 2023 – October 2023

Name:	Nia Foster		
Supervisor(s):	Dr Paul Kavanagh & Prof Peter Robertson		
Position:	PhD Student		
Start date:	2nd October 2023	**Anticipated end date:**	August 2026
Funding body:	Department of Economy		

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

Background

Oxidations and reductions are incredibly important reactions in chemistry, with their applications being used in every area. They are often carried out in dangerous solvents with harmful catalysts. Electrolysis has recently been highlighted as a successful and environmentally friendly way to carry out these reactions, however combining electrolysis with photoexcitation will potentially increase the effectiveness of these catalysts, allowing for the reactions to be carried out at higher potentials which will require less energy. To activate an electrocatalyst, a very negative potential must be applied, however the hope is once blue light is present to excite the molecule, it should be able to be reduced at a less negative potential. The aim of this process is to generate the radical anions in-situ, which will then be excited by the blue light, making them much more strongly reducing.

This area of study was popular in the 1980's with researchers such as Prof Robertson studying quinone radical photoelectrochemistry. Interest in electrophotochemistry dwindled overtime, however it resurfaced around 2019 and has gained a lot of traction in recent years.

Objective of this work

At the moment, my end goal for this project is to have a deeper understanding of electrophotocatalysis and how it works, as well as possibly reducing very hard to reduce molecules such as carbon dioxide or nitrogen, and hopefully turn them into more useful products. These processes are very expensive to carry out, so ideally this research will lead to a less energy intensive and more environmentally friendly methods of performing these reactions.

Progress to date

Currently I have been studying different electrocatalysts and finding their redox potential, diffusion coefficient and the heterogeneous rate constant for each. This is only the beginnings of my research as I plan on categorising and creating a list of these electrophotocatalysts that are all studied under the same conditions, which hasn't been carried out previously. I have tested five different molecules so far, under the same conditions, which are all shown at the end of this report. Currently I am using cyclic voltammetry to study these reactions. I have also begun research for a literature review.

Conclusions and future work

I am planning on continuing research into different electrocatalysts. Ideally, I'll be able to find catalysts that can be successfully reduced or oxidised, which I will then use to test for their activity once they have been excited using blue light. Later in my research I plan on using these electrocatalysts to try and oxidise or reduce different molecules. Through testing a collection of these catalysts, soon I will hopefully be able to categorise them by their redox potential, diffusion coefficient and the heterogeneous rate constant for myself and others to refer to. This study on these catalysts under the same conditions hasn't been carried out before so I believe it will be very helpful to have, especially as this area grows.

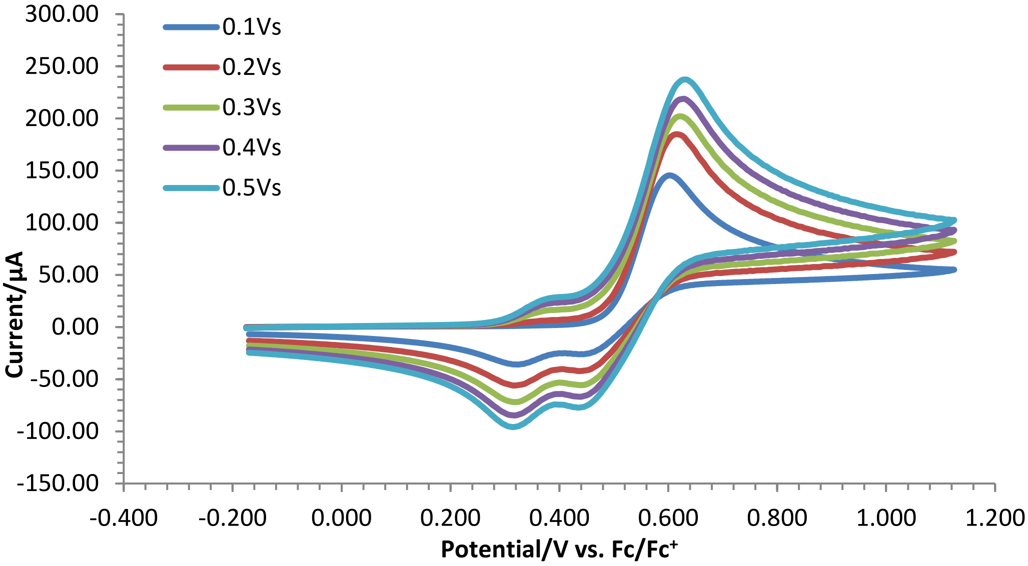
Furthermore, I am focusing on starting a literature review on previous research on electrophotocatalysts.

Results

All experiments carried out in 2ml MeCN, with 0.15MM $LiClO_4$ and catalyst concentration of 5mM.

TPA

Average E°= 0.152
Diffusion coefficient for oxidation = $5.35x10^{-6}$
Diffusion coefficient for reduction = $2.58x10^{-6}$
Heterogeneous rate constant = $7.52x10^{-6}$
CV:



TDPA

Calculations based on peak at -0.0185

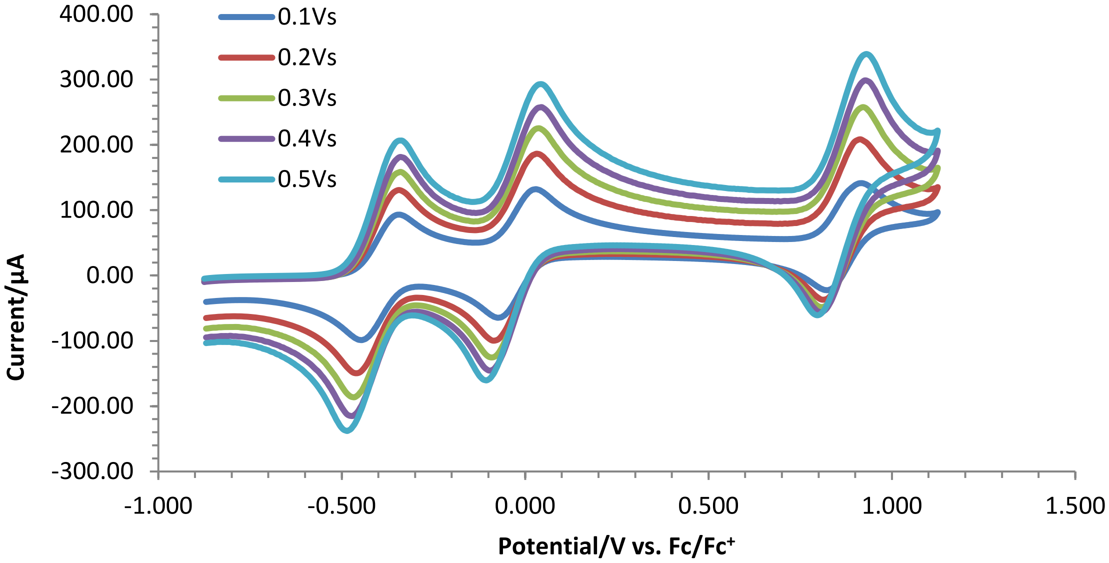
Average E°= -0.0185

Diffusion coefficient for oxidation = $1.66\text{x}10^{-5}$

Diffusion coefficient for reduction = $6.26\text{x}10^{-6}$

Heterogeneous rate constant = 0.00275

CV:



TBPA

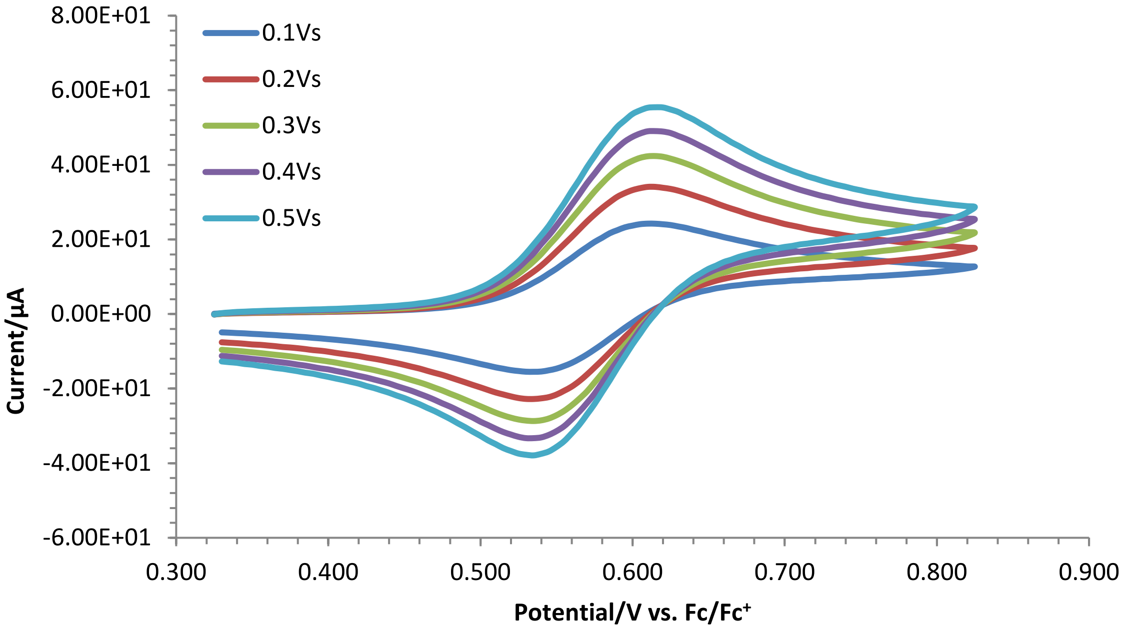
Average E°= 0.678

Diffusion coefficient for oxidation = $7.07\text{x}10^{-7}$

Diffusion coefficient for reduction = $3.59\text{x}10^{-7}$

Heterogeneous rate constant = -0.00231

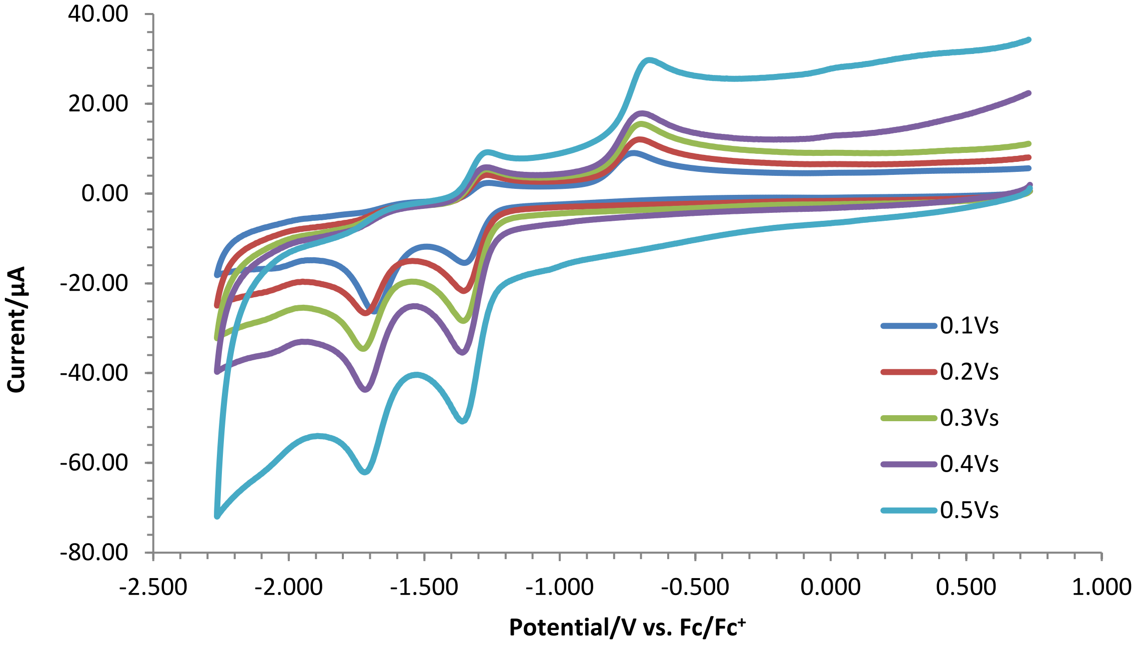
CV:



DCA

Unable to find the E°, diffusion coefficient, or the rate constant.

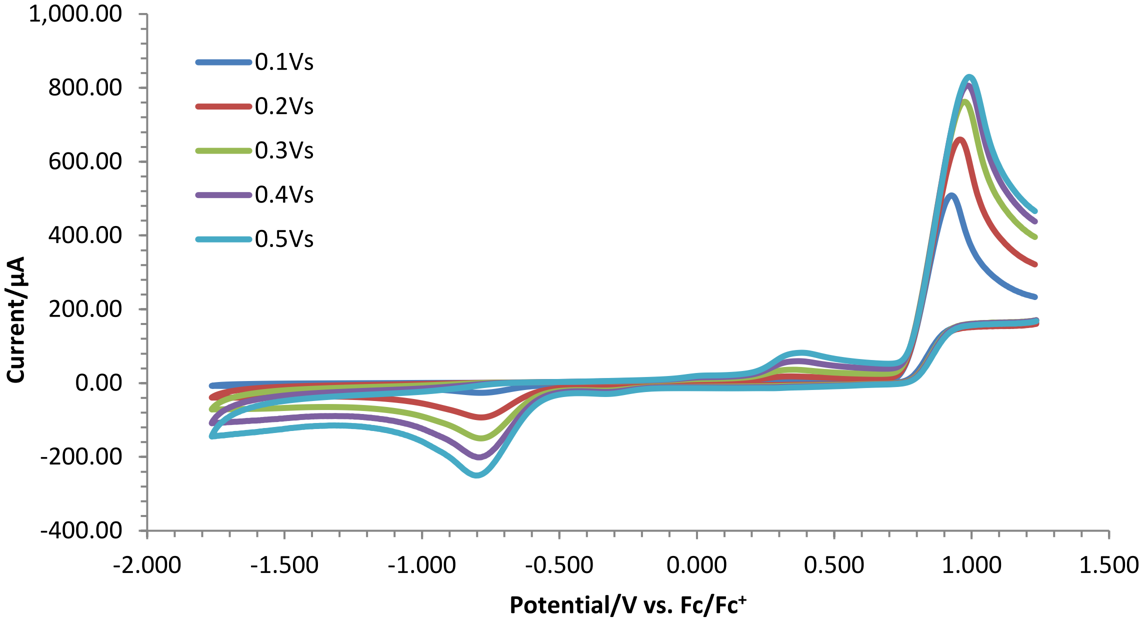
CV:



Anthracene

Unable to find the E°, diffusion coefficient, or the rate constant.

CV:



QUILL Quarterly Report

August 2023 – October 2023

Name:	Reece Gallagher		
Supervisor(s):	Prof Peter Nockemann, Dr Oana Istrate & Dr Paul Kavanagh		
Position:	PhD student		
Start date:	1st October 2023	**Anticipated end date:**	30 September 2026
Funding body:	Shell and DfE		

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

Overview of work to date

Over the last six weeks I have been conducting a thorough literature review focusing on academic papers which discussed the design and synthesis of non-vanadium electrolytes for redox flow batteries based on abundant metals. Within the six-week time period I have delivered two different presentations in front of my supervisors. In the first presentation I was given three papers to review which were relevant to my area of research and completed an analysis of each paper. I learned how important a balance between stability and solubility are for sustainable electrolytes while also gaining an understanding of how these features are measured in the lab.For my second presentation I had to select three papers myself which I believed to be relevant to my topic of research and review them. I choose to focus on some already well-established systems for iron-based complexes by comparing performance and stability results of Fe(TEA), Fe(DIPSO) and Fe(Bis-Tris) complexes and ferrocyanide as redox couple. This enabled me to gain a greater understanding of the strengths and weaknesses of each system.

Conclusions and future work

Over the last six weeks I have gained a better fundamental understanding of what different avenues are being explored in relation to developing non-vanadium electrolytes for redox flow batteries. I am currently working on developing an experimental plan in which I will use the literature review to aid me in deciding the direction of study that I will be taking.

References of papers reviewed for presentations:

1. 1M. Shin, S. Oh, H. Jeong, C. Noh, Y. Chung, J. W. Han and Y. Kwon, *International Journal of Energy Research*, 2022, **46**, 8175–8185.
2. 1M. Shin, C. Noh and Y. Kwon, *Chemical Engineering Journal*, 2023, **453**, 139738.
3. 1M. Shin, C. Noh, Y. Chung and Y. Kwon, *Chemical Engineering Journal*, 2020, **398**, 125631.
4. 1X. Li, P. Gao, Y.-Y. Lai, J. D. Bazak, A. Hollas, H.-Y. Lin, V. Murugesan, S. Zhang, C.-F. Cheng, W.-Y. Tung, Y.-T. Lai, R. Feng, J. Wang, C.-L. Wang, W. Wang and Y. Zhu, *Nature Energy*, 2021, **6**, 873–881.
5. 1K. Gong, F. Xu, J. B. Grunewald, X. Ma, Y. Zhao, S. Gu and Y. Yan, *ACS Energy Letters*, 2016, **1**, 89–93.

6. 1R. Feng, X. Zhang, V. Murugesan, A. Hollas, Y. Chen, Y. Shao, E. Walter, N. P. Wellala, L. Yan, K. M. Rosso and W. Wang, *Science*, 2021, **372**, 836–840.

QUILL Quarterly Report

August 2023 – October 2023

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

3D Printing for Renewable Energy Applications

Background

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

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

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

Objective of this work

To create a viable redox flow battery (RFB) electrode that has been manufactured through 3D-printing technology.

Progress to date

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

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

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

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

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

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

Conclusions and future work

Summarise the most important finding/conclusion to date. Where do you go next?
If you published your work, please provide reference here.

Conductive and catalytic electrode structures have now been produced using 3D printing methods. The project will continue to develop the resin 3D printing process whilst undertaking thorough characterisation of materials. Options to explore include using functionalised fillers to improve resin dispersion, utilising conductive polymers, and carbonisation of resin printed structures. Future work will also include testing of electrode structure in RFB test cells.

QUILL Quarterly Report

August – October 2023

Name:	Aloisia King		
Supervisor(s):	Prof John Holbrey & Prof Małgorzata Swadźba-Kwaśny		
Position:	PhD student		
Start date:	01 October 2021	**Anticipated end date:**	March 2025
Funding body:	EPSRC		

Intrinsic FLP Systems in Ionic Liquids

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 characterised. *N*-Alkylacridinium *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. The H_2 screening experiments, initiated previously are still under detailed investigation. We have began to collaborate with Dr. Leila Moura and her student Mark Young in order to quantify H_2 uptake by the FLP systems via the Headspace GC system that they have developed. Additionally, we began to investigate a range of Internal NMR standards that we could use in order to quantify the substrate reduction reactions that we have been carrying out using the FLP system. We have now found a suitable Internal standard and plan to carry out these reactions within the next few weeks. Also investigation has taken place to try and develop better synthetic procedures for the synthesis of the *N*-alkylated acridinium cations, as some of the procedures were low yielding and required long reaction times. As a result, new and improved methods of synthesising *N*-propyl acridinium [NTf_2] and *N*-butyl acridinium [NTf_2] have been performed. It was pivotal that we improved synthetic procedures for acquiring these materials, that were high yielding in order to utilise these LAs within an FLP IL system and Hence, in order to be able to sufficiently quantify the catalytic capabilities via Headspace GC. We also have managed to attain a single crystal structure of our EthylAc[NTf2] LA and this is a novel single crystal structure. We have submitted a proposal to carry out a Neutron scattering study on the Acid/base association in the N-methylacridinium bistrifylimide/lutidine ionic liquid Frustrated Lewis Pair and we will begin to deuterate our Intrinsically IL FLP system in anticipation that our proposal is accepted. As well as the work mentioned above, ongoing investigations are being conducted to synthesise a range of 3,5-dicyanopyridine analogues. We anticipated that this set of molecules may be able to be used as alternative cations (within an FLP system), due to their similar hydride ion affinity to that of the dihydromethylacridinium molecule [3]. However, through recent discussions we have decided that this class of alkylated 3,5-dicyanopyridines should have a good, innate ability to act as IL based charge transfer materials, as previous work on cyanopyridinium IL work within the group was successful in establishing a new class of charge transfer materials [4]. We also have decided to revisit a range of 4-Cyanopyridinium [NTf_2] that have been examined by the Group in the past as CTMs, when paired with 1-Methylnaphthalene. The aim of this work is to try and develop a deeper understanding of the charge shuttling/ transfer mechanism between these ILs and 1-Methylnaphthalene via (EIS). We are collaborating with Dr. Josh Bailey on this strand of the work. To date, we have developed an experimental setup to carry out these experiments and have done some preliminary tests on an IL to check the reliability of the experimental setup. I have been synthesising and characterizing the ILs for EIS and the experiments are planned for early December.

Conclusions and future work

We plan to carry out our substrate hydrogenation reactions utilising the suitable Internal standard in the next few weeks. Upon completion of these reactions, work will begin on probing the Fluorescent nature of the Intrinsically IL FLP system and the various LA components. Additionally, we will begin deuteration reactions of the N-methylacridinium bistrifylimide/lutidine ionic liquid FLP, in preparation/anticipation of carrying out experiments at ISIS. It is also planned that if the preliminary headspace GC samples that have been given to Dr. Leila Moura's group are successful, we will provide a range of our Intrinsic IL FLPs for them to test- so preparation is being made also to synthesise much more material. In conclusion, the last bit of work that is planned for the next while is EIS spectroscopy on the 4-cyanopyridinium ILs and after completion of the analyses of these ILs, we will move on to the 3,5-dicyanopyridinium ILs. So hopefully, we will have been able to devise synthetic procedures for these soon.

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QUILL Quarterly Report

August 2023 – October 2023

Name:	Sanskrita Madhukailya		
Supervisor(s):	Professor John Holbrey & Dr Leila Moura		
Position:	PhD student		
Start date:	April 2021	**Anticipated end date:**	April 2024
Funding body:	TU-QUB-Joint PhD Scholarship		

LCST Behaviour in 5-Phenyltetrazolate Based Ionic Liquids

Background

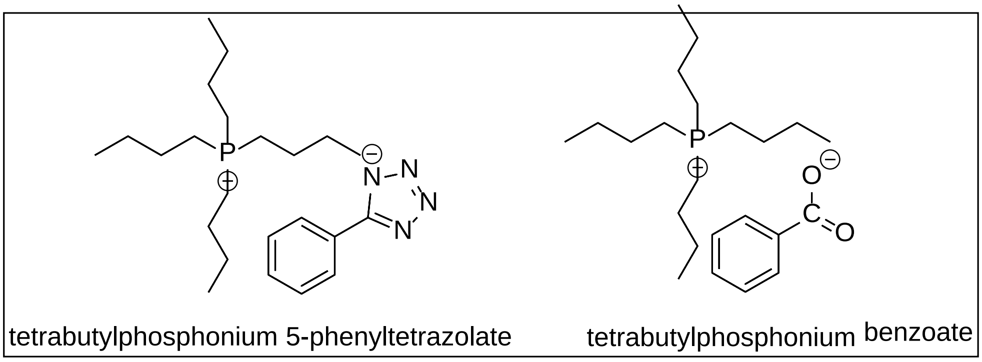
In the previous report, deuteration of tetrabutylphosphonium bromide was attempted to prepare the D-ionic liquid for neutron scattering experiments. In addition to that, posters were presented at QUILL IAB and COIL-9 conference. Herein, a brief about some of the isothermal titration calorimetric experiments that were carried out in ENS de Lyon under Professor Margarida Costa Gomes, are reported. This was done with an intention to understand the thermodynamics of the LCST systems by quantifying the energies of hydration and comparing them to non-LCST behaviours.

Objective of this work

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

Progress to date

Experimental: The ionic liquids tetrabutylphosphonium 5-phenyltetrazolate, $[P_{4444}][PhTet]$ and tetrabutylphosphonium benzoate, $[P_{4444}][Bnz]$ were synthesised using reported methods and HPLC Plus grade water was supplied from Sigma-Aldrich. The chemical structures of the two ionic liquids studied in this work are represented in *Figure 1*.



tetrabutylphosphonium 5-phenyltetrazolate   tetrabutylphosphonium benzoate

Figure 1 - The ionic liquids, $[P_{4444}][PhTet]$ (left) and $[P_{4444}][Bnz]$ (right), under study for isothermal titration calorimetry experiments.

Instrumentation: An isothermal titration calorimeter (TA instruments) equipped with a thermal activity monitor (TAM) III thermostat (TA Instruments) was used for measuring the mixing enthalpies (ΔH_{mix}) at atmospheric pressure and at 298.15 K. Two cells of 1ml were used: one of them containing the sample (working cell) and the other reference cell. During the titration experiments, small volumes (1 to 5 *μl*) of ionic liquid-water mixture or pure water, according to the conditions, of a known composition were injected (from a 250 *μl* syringe) into the working cell. To ensure an effective mixing, the liquid in the cell was stirred at 60 rpm. A motor-riven pump was used for the automatic injections (18-22 per experiment), each one during 30 to 90 s. Between them, an interval of 180 mins was established to allow baseline recovering.

After each injection, a peak corresponding to the heat effect of the mixing process was recorded. The area of the peak, Q, is proportional to the heat involved, and is the value required for the enthalpy of mixing calculations. The whole apparatus is connected to a computer by which we can program calibrations, injections and calculations of the heat involved in each addition.

Results and discussion: The area of the peak observed for each injection of the sample determines the Q per moles of the solute added. *Figure 2* represents an example of the integrated value of the heat released (Q in mJ) during the second injection of the sample, $[P_{4444}][PhTet]/H_2O$ at 3.6953×10^{-6} moles of the ionic liquid in 8.30556×10^{-5} moles of water at 298.15 K.

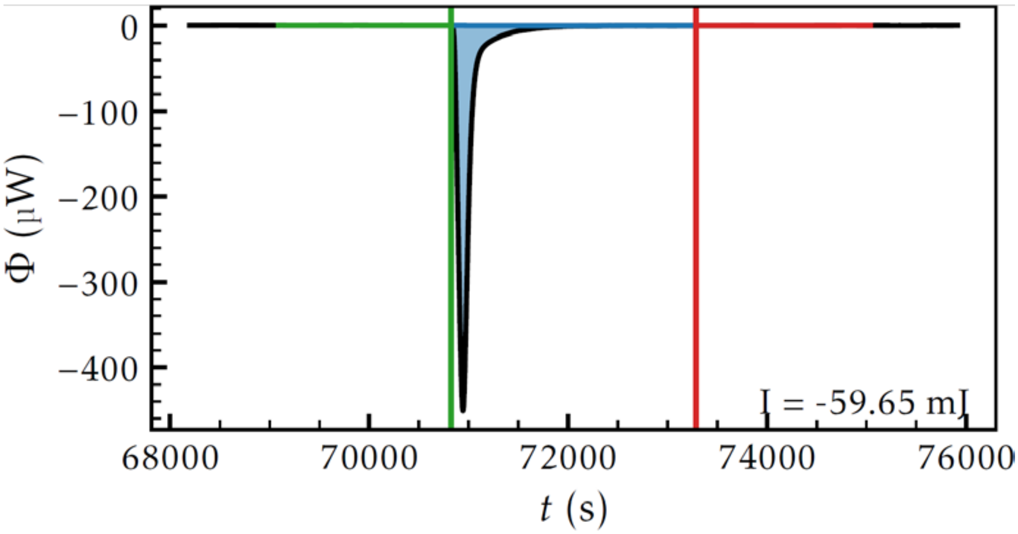


Figure 2 - Integrated value of the heat released on the second injection of the sample $[P_{4444}][PhTet]/H_2O$ (syringe), to H_2O (cell)

Different compositions of the mixtures of both the ILs with water were prepared and tested for their energies involved during the mixing process. It was observed that for the LCST ionic liquid, the heat involved somewhat remained the same for the different compositions studied, whereas, for the non-LCST IL, tetrabutylphosphonium benzoate, the heat involved changed drastically as the compositions were varied. (Data not included.)

Future works

1. Complete ITC experiments at 65°C and analyse results for a paper.
2. Complete deuteration of the cation for neutron scattering experiments, to be included in the paper.
3. Complete the thermophysical characterisation of the mono and dicationic ionic liquids for two other papers.

QUILL Quarterly Report

August 2023 – October 2023

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

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

Background

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

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

Objective of this work

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

Progress to date

Throughout the last quarter the primary focus has been on the synthesis of literature and the writing of a review paper which is now largely complete with the first round of internal review now underway. This paper looks at the areas of early detection for lithium-ion cells as well as the use of interstitial materials for both thermal runaway prevention and thermal management.

Discussions are ongoing around the possibility of physical testing being conducted at MIRA, as this would be a significant boost to the project.

The first steps in converting an earlier developed 2D MATLAB model into a 3D Multiphysics model have begun.

Conclusions and future work

The review paper will require a few more revisions after internal review before hopefully being submitted to a journal before the end of the year. Focus will then switch to modelling efforts as the next main work package.

QUILL Quarterly Report

August 2023 – October 2023

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

As I just started my PhD project on 14th August, I mainly spent this quarter introducing myself to the project as well as safety procedures, lab equipment and instrumentation. I started by conducting a literature review to familiarise myself with the project and the theory behind it, I focused on many different topics including: ionic liquids, Lewis acidity of boron, neutron scattering, X-ray absorption spectroscopy (XAS), X-ray Raman spectroscopy (XRS) and Frustrated Lewis Pairs. I also completed safety training for liquid nitrogen and gas cylinders.

Subsequently I started to familiarise myself with DISSOLVE, a new simulation software to analyse and model neutron scattering data.

I then performed a deuteration experiment on $[P_{66614}]Cl$ using a carius tube and under an argon atmosphere, and I am continuing to work this up. Deuterations are very important for neutron scattering as it provides multiple sets of data for the same sample, so that you can compare. This will be sent to our collaborators for analysis.

I attended the QUILL meeting and then travelled to ISIS and Diamond in Oxfordshire, England. At ISIS, I assisted Harris Amir with his experiment on the instrument SANDALS, and then at Diamond, using beamline I20 helping Beth Murray with her experiment involving EXAFS. Whilst I was there, I met with Dr. Luke Higgins who introduced me to python, and it is how we analyse the data from XRS. Since returning I have continued to work on this and learning python and analyse the data which was captured at the European Synchrotron Radiation Facility (ESRF) on beamline ID20 in February 2023.

Subsequently I have been conducting another deuteration experiment with 1-methylimidazole using the microwave, which was successful, it took time to work out the reaction conditions, after that I ran the reaction in batches and combined them. This sample will also be sent to our collaborators at Imperial College London.

The main things I have completed is the two deuteration synthesis reactions and learning these valuable techniques and secondly, learning python was vital as it is key for XRS data processing, these will both feature frequently throughout the course of my PhD project.

Conclusions and future work

In conclusion, I have just started my PhD and have spent time familiarising myself with the project and understanding the theory behind it, as well as learning the equipment and laboratory procedures. I made a trip to Diamond and ISIS where I will be returning frequently throughout the course of my PhD. I have also started a deuteration experiment and have been introduced to important data processing techniques.

Going forward, I will be working up the deuteration reactions, purifying and sending them to our collaborators for further analysis, I will be returning to Diamond in January to compete a soft X-ray and I will be continuing to work through the data analysis for the XRS experiments.

QUILL Quarterly Report

August 2023 – October 2023

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

Inorganic Chemistry of Group 13 Elements in Sustainable Uses

Background

This section of my PhD project is a continuation of my MChem project, that focuses on the recovery of gallium metal from the zinc manufacturing industry, specifically zinc leachate solution, using hydrophobic deep eutectic solvents (DESs).

Global demand for gallium has rapidly increased over the past two decades, due to its applications in electronic devices. Challenges in its supply are exasperated by the lack of gallium ore, with this metal being recovered as a secondary element from mine tailings of other metal industries, chiefly aluminium, although recovery from zinc mine tailings is also potentially possible.[1] Finally, gallium supply is endangered by geopolitical consideration, with the majority being supplied by China (80%).[2]

As mentioned, this work focuses on the separation of gallium from zinc leachate solution, due to in Northern Ireland, this route of recovery being of great interest, on account of Europe's largest zinc mine being located in County Meath, Ireland.[3]

Hydrophobic DESs are based on the knowledge of hydrophobic ionic liquids and share similar characteristics such as long alkyl chains to promote hydrophobicity, however, are deemed less challenging and cheaper to prepare.[4] Previous literature on hydrophobic deep eutectic solvents (DESs) present hydrogen bond acceptor (HBA) molecules in combination with hydrogen bond donor (HBD) molecules, such as a carboxylic acid. A HBA molecule of great interest is trioctylphosphine oxide (TOPO), due to its application as a metal extractant in industry,[5] as well as its long alkyl chains which promote hydrophobicity. Although TOPO is used in aqueous organic liquid-liquid extractions, a major limitation to the process is its low solubility in hydrocarbon solvents, such as kerosene,[6] which are the chosen solvents for industrial extraction processes. By incorporating TOPO into a DES, it allows for large amounts of the phosphine molecule to be concentrated in the liquid form.

Objective of this work

The aim of this work is to explore hydrophobic DESs as a route for the extraction and recovery of gallium from the zinc manufacturing industry. Our strategy relies on the use of hydrophobic DESs as cost-effective, bifunctional solvents for the extraction of gallium. The overall aim is to find a system that results in the optimum amount of gallium being recovered, along with high gallium selectivity over competitive metals in the simulated zinc leachate.

Previous recovery of gallium from zinc waste residue at the zinc plant in Porto-Maghera yielded low level recovery of gallium, as well as involving high energy consumption, lengthy procedures, and the risk of secondary pollution. Additionally, the incorporation of polyphenols, compounds associated with potential toxicity and various safety considerations, raises significant concerns.

Another process presented by Zhang et al. includes the use of sulfonated kerosene as a diluent for Cyanex® 272. Although kerosene is considered 'more eco-friendly' than other fossil fuels, it still has environmental and safety disadvantages. In comparison to these previous methods, this work targets the objective of extracting and recovering gallium via an environmentally benign process.

Progress to date

In this work we use a mixture of trioctylphosphine oxide (TOPO), a common component in industrial metal extractants and malonic acid, a naturally occurring compound, to form a hydrophobic deep eutectic solvent (DES) to selectively recover gallium from zinc leach residue. By incorporating TOPO into a DES, it allows for high concentrations of TOPO (the extractant molecule) to be in the liquid form. This addresses a prior challenge as TOPO traditionally exhibits low solubility in organic solvents, which are essential for organic liquid-liquid extractions.

Hydrophobic DESs exhibit similar properties to hydrophobic ionic liquids (ILs), however, are cheaper and easier to prepare. Synthesis of a DES is a very simple process, which involves adding the two components together and heating to ~ 60 °C whilst stirring until a homogeneous liquid is formed. Therefore, in this invention we present a TOPO:malonic acid hydrophobic DES as a green, cost-effective solvent for the extraction and recovery of gallium from zinc leach residue.

To study the TOPO:malonic acid DES as a gallium extractant, a model feedstock solution was made to mimic real zinc leach residue. The concentration of metals in the model feedstock are shown in Table 1. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was the technique used to determine each metal concentration.

Table 1 - Concentration of metals in zinc leach residue feedstock

Metal	Theoretical zinc leachate concentration (ppm)[7]	Initial concentration of multi-metal stock solution (ppm)
Zn	9300	103500
Fe	4200	4980
Al	4500	5000
In	960	914
Cu	261	258
Ga	36	42

The zinc leachate model feedstock poses significant challenges owing to its low initial gallium concentration and the presence of high concentrations of competitive metals, particularly iron and copper, which share chemical similarities with gallium. The multi-metal zinc leachate feedstock solution was contacted with the TOPO:malonic acid extractant and the metal content in the aqueous phase determined pre- and post-extraction using ICP-OES analysis. During the extraction experiments, the extractant was initially mixed with the zinc leachate solution for a duration of 30 minutes. However, a test was conducted to evaluate the impact of reducing the contact time to 10 minutes on the coextraction of metals. Surprisingly, it was discovered that the extraction efficiency for all metals remained the same, indicating that equilibration of the system had already been achieved within 10 minutes. As a result, the extraction contact time was subsequently shortened to 10 minutes. To establish a benchmark, a TOPO:malonic acid system (χ_{TOPO} = 0.60) was employed based on prior research. This previous study demonstrated that all metals in the model feedstock exhibited 100% extraction.

After the completion of the extraction studies, attention was directed towards the potential to recover gallium from the eutectic phase while minimising the co-stripping of other metals. Previous work on back-extraction stripping agents had found 0.5 M HCl, and both 0.5 M and 1.0 M NaOH not to be efficient gallium stripping agents. This resulted in 1.0 M NH_3(aq) as a metal-free, organic base being selected as a stripping agent, in which previous studies showed its success in the recovery of gallium from the organic TOPO:malonic acid phase. An overall process flow diagram for gallium recovery from the model zinc leachate solution feedstock is shown Figure 1.

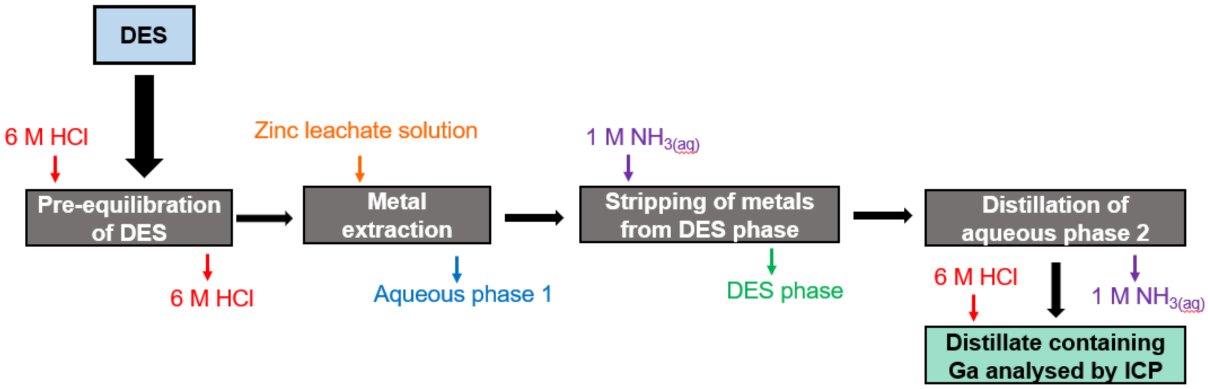


Figure 1 - Process flow diagram showing the process of gallium recovery from model zinc leachate solution feedstock using DES

The extraction study highlighted the substantial coextraction of competitive metals, which prompted the investigation into minimising their stripping from the organic eutectic phase into the aqueous phase during gallium recovery. Stripping experiments conducted on the TOPO:malonic acid system (χ_{TOPO} = 0.60) show gallium can be successfully recovered from the eutectic phase using 1 M NH_3(aq) solution (8.4 ppm). In contrast, a drawback of this system was the co-recovery of iron and copper. On the other hand, no traces of aluminium, indium, or zinc were detected in the aqueous phase following the stripping process.

Based on insights from existing literature, we opted to introduce a low concentration of ascorbic acid (commonly known as vitamin C), a natural reducing agent, and a small quantity of water into the TOPO:malonic acid system. Both the ascorbic acid and water were added to the hydrophobic DES system as additives. This concept was motivated by the potential of ascorbic acid to reduce Fe^{3+} to Fe^{2+} and/or Cu^{2+} to Cu^{+}, effectively transforming both iron and copper into forms less similar to gallium. The TOPO:malonic acid (χ_{TOPO} = 0.60) hydrophobic DES with the addition of ascorbic and water, yielded favourable outcomes. It not only enhanced the system's selectivity by preventing the simultaneous recovery of copper but also increased the gallium recovery to approximately 60%. %. A table of results showing metals recovered from TOPO:malonic acid with ascorbic acid and water is shown in Table 2. A total metal mass balance for the newly modified system with ascorbic acid and water is also shown in Figure 2.

Table 2 - Amount of each metal from the zinc residue feedstock recovered in the final aqueous phase using TOPO:malonic acid (χTOPO = 0.60) with the addition of ascorbic acid (0.15 mol dm-3) and water (2.5%)

	Al	Cu	Fe	Ga	In	Zn
Model feedstock (ppm)	5000	258	4980	42	914	10350
Recovered aqueous phase, χ_{TOPO} = 0.60 TOPO:malonic acid + ascorbic acid + water (ppm)	22	10	2713	26	3	3
% of metal recovered	0.4	3.9	54.5	61.9	0.3	~0

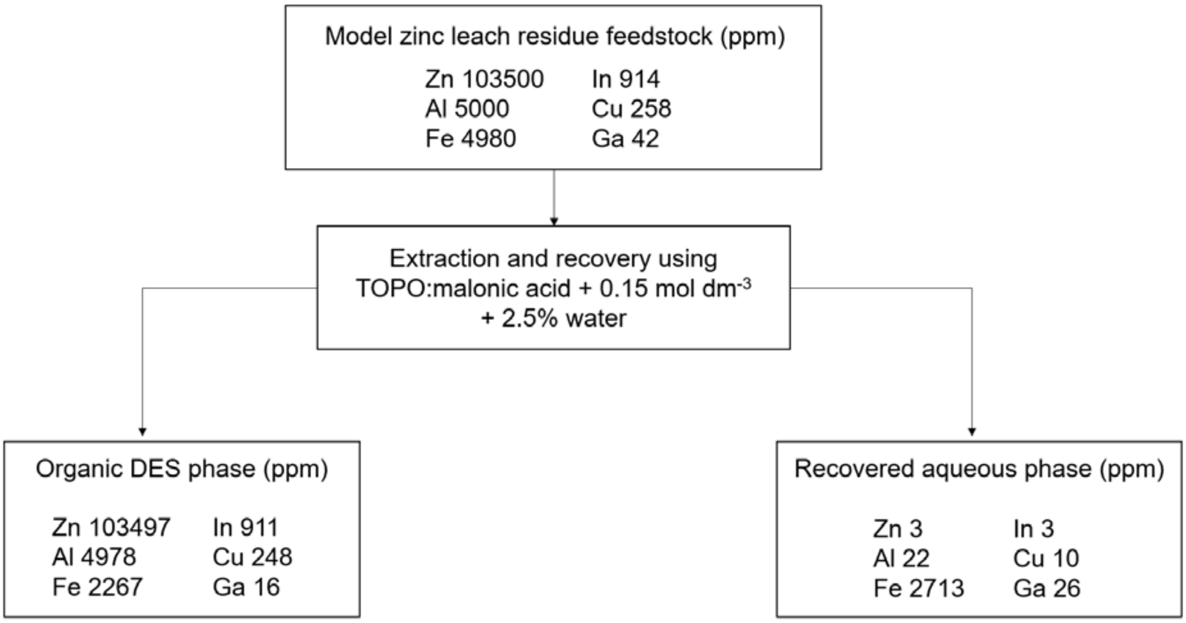


Figure 2 - Total metal mass balance for the extraction and recovery process using TOPO:malonic acid (χ_{TOPO} = 0.60) with 0.15 mol dm^{-3} ascorbic acid and 2.5% water additives. Concentrations are given in ppm

As previously mentioned ascorbic acid has been added to the system due to literature findings which propose it has the ability to reduce Fe(III) to Fe(II) and Cu(II) to Cu(I), with the rational for reducing both iron and copper to try and prevent their recovery from the eutectic phase, and further improve the gallium selectivity of the system. Both Fe(III) and Cu(II) have similar tetrahedral and octahedral ionic radii to Ga(III), which is a possibility as to why competitive metal co-extraction takes place. Up until now it is assumed the reduction of these metals to their lower oxidation states results in a change in their ionic radii, making them more dissimilar to Ga(III), the target metal to be recovered. Although literature suggests this process is likely to happen, there is a gap in the knowledge of what happens to the oxidation state and coordination chemistry of the metals throughout the process. In order to investigate this we recently attended beamtime at Diamond Light source in October. At this beamtime we investigated the speciation and coordination environment of gallium, copper, iron and zinc in different stages throughout the process. By doing this it allows us to determine what environment and oxidation state each metal is in each step of the process, helping to explain why ascorbic acid makes a difference to the process.

Conclusions and future work

We have successfully developed a method for gallium recovery from a model zinc leach residue feedstock utilising a hydrophobic deep eutectic solvent. Our approach involves fewer steps and employs environmentally benign and cost-effective chemicals compared to previous methods used for gallium recovery from zinc waste. The incorporation of the natural reducing agent, ascorbic acid, and water into the well-characterized hydrophobic deep eutectic solvent, TOPO:malonic acid (χ_{TOPO} = 0.60), has significantly improved the system's selectivity by reducing the co-stripping of copper. Additional efforts are necessary to further optimize this system, as previously mentioned, particularly focusing on the separation of iron and gallium in the final recovered aqueous phase.

Future work includes the processing of EXAFS data obtained on I20 beamline at Diamond, to obtain information on the oxidation states and coordination environment of gallium, iron, copper and zinc throughout the extraction and recovery process. Other future work includes some small experiments to determine optimum conditions for gallium recovery, including altering the concentration of ascorbic acid/water added.

Other future goals include securing IP and applying for an iCure Explore programme delivered by NxNW, as a possible route for this work is the creation of a spin-off company. Our vision is to build a spin-out around a technology that is socially acceptable in developed countries, contributes to security of supplies and does not involve, at any step, countries of high risk (as specified in UK Critical Elements policy from July 2022). Within five years, we would like to have a pilot-scale plant with robust data on continuous flow process working on real-life feed from partnering zinc mines.

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QUILL Quarterly Report

August 2023 – October 2023

Name:	Michael Sweeney		
Supervisor(s):	Dr Leila Moura & Prof John Holbrey		
Position:	1st Year PhD student		
Start date:	October 2023	**Anticipated end date:**	October 2026
Funding body:	CAST DfE & Chevron		

CO2 Capture from Commercial Flue Gas Process Streams

Background

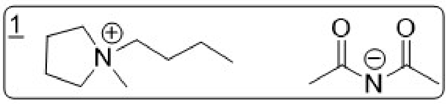
As the ever-increasing effects of climate change can be seen across the globe it is imperative to reduce CO_2 emissions in environmental and energy friendly ways. The current technology for the removal of CO_2 from commercial flue gas is reliable upon energy intensive amine scrubbers.[1] The aim of this project is to develop new technologies that have the capacity to replace the amine scrubbers.

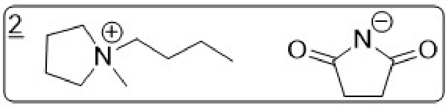
Objective of this work

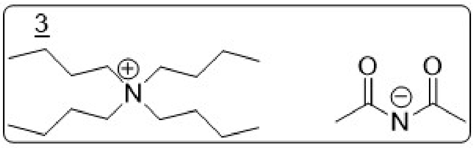
Develop and optimise ionic liquids and other technologies for treatment and removal of CO_2 from commercial flue gas process streams.

Progress to date

Currently conducting a literature review around the current state of the art processes for flue gas treatment and ionic liquids & low melting mixtures previously reported to have high solubility for CO_2 and assessing the impact of the presence of water in various concentrations[2,3]. Compiling a database of literature measurements around different anions/cations & low melting mixtures to determine their corresponding behaviours in the presence of CO_2. Categorized by whether they exhibit physisorbent or chemisorbent properties.







Experimentally, currently working on synthesis three super basic IL's[4] to test their absorption of CO_2;

1. N-butyl-N-methyl pyrrolidinium diformylamide **(P_{14}-DFA)**

2. N-butyl-N-methyl pyrrolidinium succinimide **(P_{14}-Suc)**

3. Tetrabutylammonium diformylamide **(TBA-DFA)**

Conclusions and future work

There is a vast amount of conceptually valid technologies for CO_2 capture but where scalability and industrial viability is questionable. These will then be characterised and potential gas uptake in three different water content environments (done dry, damp & saturated) will be studied. They'll initially be probed with pure CO_2 and then possibly CO_2/N_2 mixtures. Testing will be done via the via GC screening method along with a fourth DBU based IL.

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QUILL Quarterly Report

August 2023-October 2023

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

Gas Separation Technologies

Background

Biogas is a renewable and carbon neutral energy source obtained through anaerobic digestion (AD) of organic waste. Biomethane is obtained through the upgrading of biogas produced from anaerobic digesters. It consists of mainly methane and carbon dioxide with many trace compounds including hydrogen sulfide, ammonia, silioxanes, terpenes and water vapour. Biomethane must be of a purity equal to or better than that of natural gas if it to be utilised for grid injection therefore a methane purity of above 96% must be achievable from any prospective technology. Carbon dioxide should make up 2.5-4% of the remaining volume with contaminants such as sulfur and siloxanes being limited to 10 mg/m^3 and 0.1 mg/m^3 respectively. The primary focus of this research is on carbon dioxide/methane separation as these are the two major components of biogas.[1]

Currently biogas upgrading is multistep, with scrubbing used for carbon dioxide removal from the biogas stream to concentrate methane. This involves the use of liquid amines such as MEA (monoethanolamine) where carbon dioxide is captured through a chemisorption process. Regeneration of the amines requires high energy inputs in the form of steam at 100-150^{o}C to reform the initial liquid amine. Water scrubbing can also be used but this requires large amounts of water and leads to methane slip due to the lower selectivity of water compared with other technologies. Membranes offer another option for upgrading but these also suffer from a range of issues such a low throughput coupled with fouling and plasticisation. The degradation of membranes leads to issues both economically in the form of having to replace them but from an environmental standpoint it is unsustainable to continuously have to dispose of and manufacture replacement membranes. Cryogenic distillation offers a method of using nontoxic materials to produce high purity gas streams through the utilisation of low temperatures and high pressures which allows carbon dioxide to liquefy leaving a pure methane stream. However the energy cost associated with this method is massive which makes it less sustainable and exceedingly costly.[2]

It is for these reasons that we seek to create novel materials which will be more efficient, more sustainable and economically viable for biogas upgrading. Initial work will consist of the use of deep eutectic solvents in conjunction with other materials to increase their upgrading capabilities.

Work to date

Gas screening methodology

Measurements to quantify the gas capacity and selectivity of both liquids and solids can be painstakingly slow and have a high associated cost. I have been developing a headspace GC (HS-GC) methodology to quickly screen liquid and solid sorbent materials for their gas capacity and separation ability. The screening can be performed at a range of pressures and temperatures, with a variety of pure gases and mixtures of gases. To do this I tested multiple combinations of HS-GC vials, stoppers and caps, resulting in the combination described in figure 1. The idea is to use the vials as mini equilibration vessels in which PVT based measurements can occur. These measurements are not expected to be as accurate as other methods, but we expect them to serve for screening purposes.

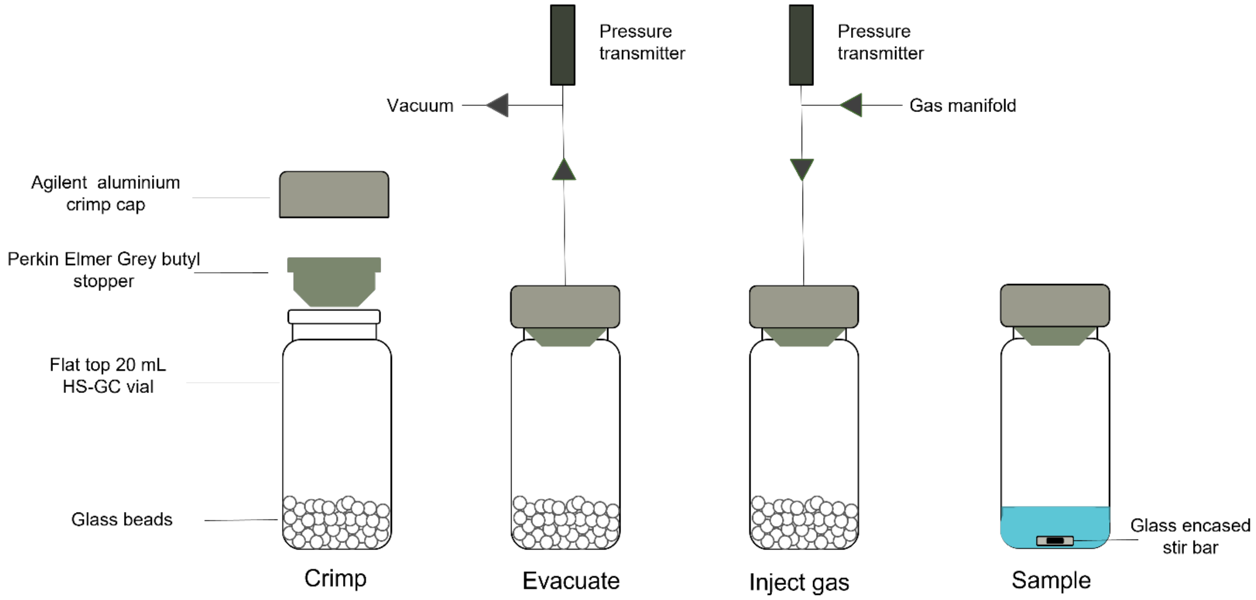

Figure 1 - Schematic of HS-GC vial preparation for calibration (glass beads) or for gas uptake measurements with sample (blue liquid)

By injecting a known "initial pressure" (quantity determined by PV calculations) of pure gas into an evacuated HS-GC vial we can compare the peak area associated with the injected gas from a calibration curve to the recorded peak area after equilibration with a known sorbent. The pressure difference in these two values equates to the gas uptake. An example can be seen below in figure 2 where a variety of CO_2 uptake isotherms of initial pressure against peak area shows that decreased peak areas can be seen in materials with a higher associated gas capacity. We have recently improved the method to allow for a triplicate of vials to be prepared in as little as 3 minutes by altering some experimental conditions.

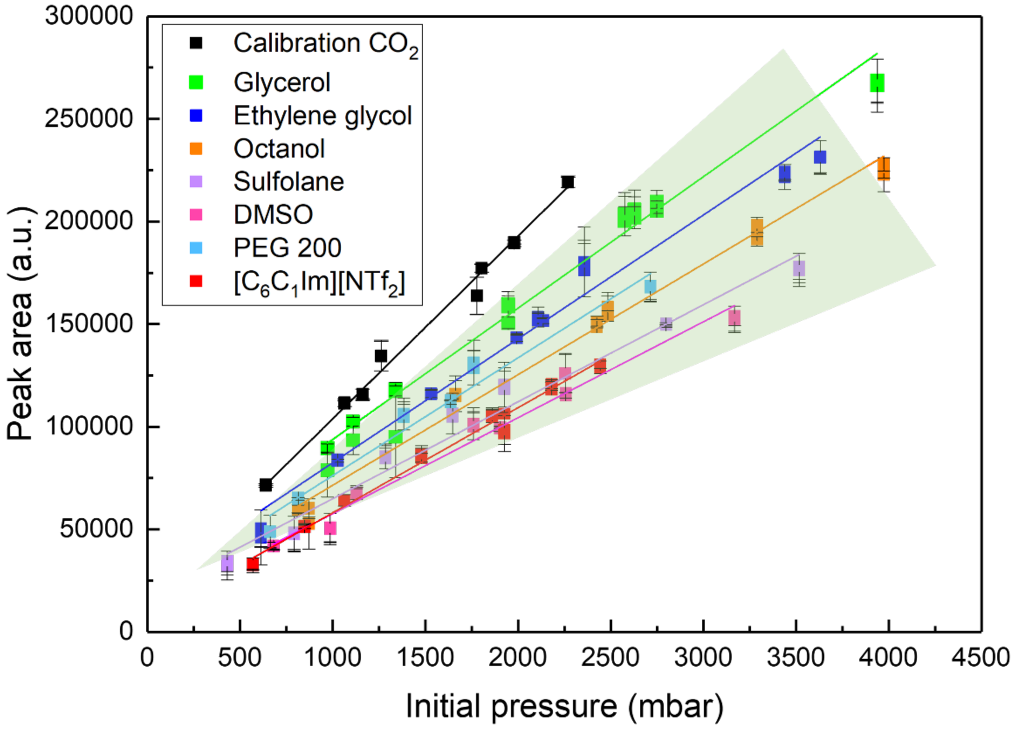

Figure 2 - Comparison of peak areas associated with different materials after equilibration with a known initial CO_2 pressure when compared to a calibration curve using glass beads[3–6]

This data was then converted to mole fraction as a function of equilibrated pressure and compared to literature data for the same materials (fig 3). It can be seen that the experimental gas capacities using this method are in good agreement with that of the literature data within the same pressure range.

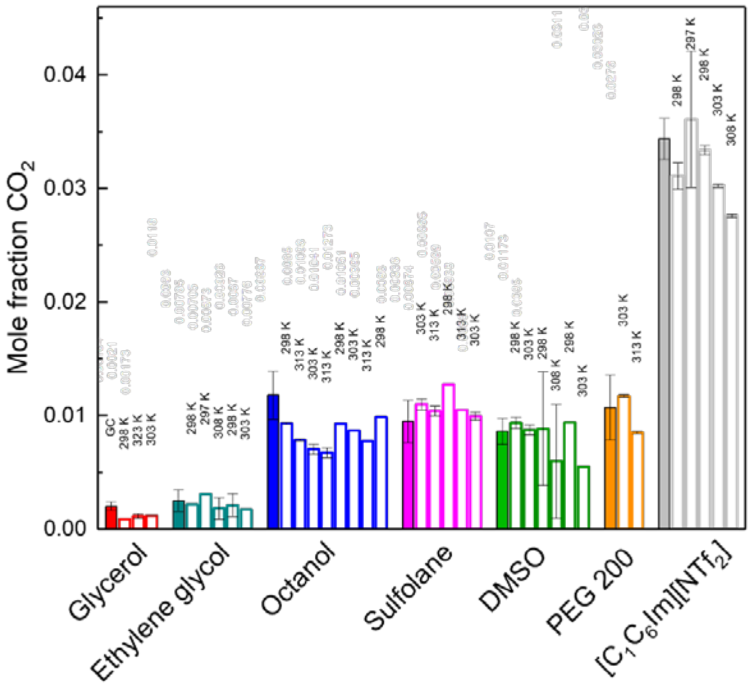

Figure 3 - Experimental uptake data of mole fraction of CO$_2$ obtained at 1 bar in this work (Solid colour) when compared with uptake data from literature sources (hollow bars) showing good agreement with literature data [3–6]

The same experiments have also been carried out with high capacity materials such as zeolites, molecular sieves, porous liquids and chemisorbing solutions. All materials showed good agreement with that of the literature.

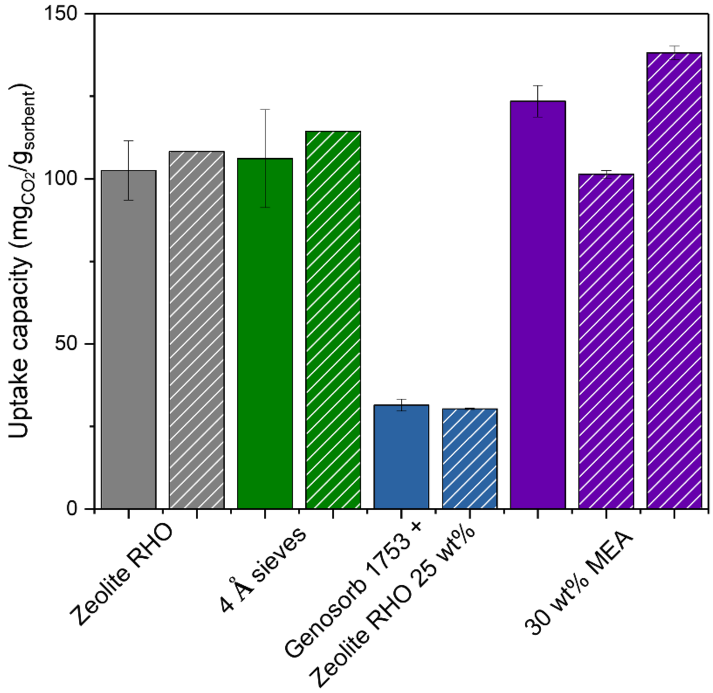

Figure 4 - Experimental uptake data of mole fraction of CO$_2$ obtained at 1 bar in this work (Solid colour) when compared with uptake data from literature sources (white stripes) showing good agreement with literature data[7–10]

Measurements like these have been carried out with CO_2, CH_4, C_2H_4 and C_2H_6 so far with both solid and liquid systems. These have also been found to yield results which compare well to that of literature. The error, accuracy and deviations from the literature data for these measurements is also being estimated.

Future work

A paper regarding this work has been accepted to ACS sustainable chemistry and engineering. Work using this method to quantify hydrogen uptake is currently underway.

Work with phosphine oxide based low melting mixtures is also underway and will be the focus of my next quarterly report.

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